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Adsorptive Desulfurization of Model Oil and Commercial Diesel Using Acid-Activated Libyan Bentonite: Adsorption Behavior, Kinetics, and Thermodynamic Analysis

Ebtehal Salman[1] | Wael Elhrari[2] | Omar Sultan[1]* | Awatif Meelad[1] |
Nadya H. Al-Sbani[1] |Riyad Mahfud[3]

[1]Department of Chemical Engineering, Faculty of Oil, Gas and Renewable Energy Engineering, University of Zawia, Libya.
[2]Libyan Polymer Research Center, Tripoli, Libya.
[3]International College of Engineering and Management, Muscat, Sultanate of Oman.

ABSTRACT

Purpose: To evaluate thermally and chemically activated Libyan bentonite as a low-cost adsorbent for sulfur removal from thiophene model oil and commercial diesel, and to identify operating conditions and adsorption behavior.

Materials and Methods: Bentonite was thermally treated at 100 and 200 °C and acid-activated with 5 or 10 M HCl. Raw and activated materials were examined by XRD, FTIR, and TGA. Batch tests used thiophene in nonane and commercial diesel, with temperature, pH, contact time, and adsorbent dose varied. RSM, Langmuir/Freundlich isotherms, thermodynamic analysis, and pseudo-first-/pseudo-second-order kinetics were applied.

Results: The 100 °C/5 M HCl treatment gave the best screening performance. For model oil at pH 7, sulfur removal reached 94.0% at 120 °C and 60 min (qe = 7.05 mg/g). Using 1 g of adsorbent. For commercial diesel (261 ppm S), the highest one-factor experimental removal was 70.49% at 80 °C, pH 7, 2 g adsorbent, and 60 min. The model compound followed Langmuir behavior (R^2 = 0.9956), whereas real diesel followed Freundlich behavior (R^2 = 0.991). Thermodynamic analysis indicated endothermic, non-spontaneous adsorption for sulfur in both systems. Pseudo-second-order kinetics provided the better mathematical fit.

Conclusion: Acid activation substantially improved bentonite performance, but the lower response in real diesel demonstrates the effect of fuel-matrix complexity. The RSM model was statistically significant but showed significant lack-of-fit, so its numerical optimum should be interpreted cautiously. *(J Multidiscip Eng 2026;1:76-86)*

Keywords: Activated bentonite, adsorptive desulfurization, diesel, thiophene.

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*Corresponding author:
Omar Sultan
Email: sultan@zu.edu.ly

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1. INTRODUCTION

In recent years, increasing attention has been directed toward the development of sustainable materials and technologies for pollutant remediation and the reduction of environmental impacts associated with industrial activities. Many studies have focused on utilizing natural, locally available, and chemically modified materials as low-cost alternatives for removal, separation, and environmental treatment processes. Previous research has demonstrated the potential of natural biological materials for contaminant removal through biosorption from aqueous solutions, while other studies have investigated the extraction of functional materials such as cellulose from native

Libyan plant species to promote sustainable utilization of renewable resources and waste materials. In addition, chemical modification of polymeric materials has been explored to improve their properties for environmental applications, including oil/water separation. Alternative physicochemical treatment approaches, including electromagnetic treatment.[1-4] Recent studies have highlighted the role of modified polymer-based materials and additives in enhancing functional properties of advanced composites and improving petroleum-related processes, including crude oil flow performance.[5,6]

Sulfur-containing compounds in petroleum fuels pose a persistent refining and environmental challenge because combustion of sulfur-bearing fuels contributes to sulfur oxide emissions, particulate formation, and acid deposition. Conventional hydrodesulphurization remains the dominant industrial route, but it requires elevated temperature and hydrogen pressure and becomes less effective for refractory aromatic sulfur compounds. Adsorptive desulfurization has therefore received sustained attention as a lower-complexity alternative that can operate without hydrogen and use inexpensive mineral adsorbents.[7-10]

Clay minerals, particularly bentonite and montmorillonite, are attractive adsorbents because of their layered structure, cation-exchange capacity, surface acidity and availability. Acid or thermal activation can modify the surface, pore environment, and thereby change adsorption performance. Previous studies have demonstrated sulfur removal with natural, acid-activated and metal-modified bentonites, while emphasizing the strong influence of adsorbent composition and sulfur-compound structure.[11-16]

The present study investigates Libyan bentonite activated by thermal and hydrochloric acid treatments and applies the optimized material to a simplified Thiophene-in-nonane model oil and commercial diesel. The work combines material characterization with one-factor experiments, response-surface analysis, equilibrium isotherms, thermodynamics, and adsorption kinetics. This design permits direct comparison between a single sulfur compound and the more complex matrix of real diesel.[12-18]

The objective was to identify practical operating conditions while testing whether the same adsorption model and trends describe a real fuel matrix. This distinction is important because high performance in a model solution can overestimate practical performance when several sulfur species and competing hydrocarbons are present.[14-18]

2. MATERIALS AND METHODS

2.1 Materials and adsorbent preparation

Bentonite clay was obtained from Al-Jawf Company for Manufacturing, Distribution of Raw Materials, and Commercial Agencies, Misurata, Libya. The material was washed with distilled water, dried at 100 °C for 24 h, ground, and sieved to < 75 µm. Thermal activation was performed at 100 °C for 24 h or 200 °C for 6 h. Chemical activation used 5 and 10 M HCl at an acid-to-clay ratio of 1:10; the suspension was stirred at 240 rpm and 70 °C for 4 h, filtered, washed to pH 5, dried at 100 °C for 12 h, and sieved .The baseline dosage for all preliminary experiments and RSM modeling is 1 g/15 mL; the diesel study optionally included an experiment increasing the dosage to 2 g/15 mL to address the complexity of commercial fuel and enhance removal efficiency.[19-23]

2.2 Characterization

XRD was used to evaluate mineralogical and structural changes. FTIR was performed with a Bruker Tensor II at 4 cm^{-1} resolutions, 16 scans, and 4000–500 cm^{-1}. TGA was performed from 25 to 600 °C at 10 °C min^{-1} under nitrogen using a BAXIT BXT-TGA101 analyzer.[24-26]

2.3 Batch adsorption experiments

For the model system, Thiophene in nonane was prepared at 500 ppm. In each batch experiment, 1 g activated bentonite was contacted with 15 mL solution at 400 rpm. Temperature was varied from 25 to 120 °C, pH was adjusted to 5, 7 or 9, contact time was 15–120 min, and equilibrium experiments used 100–500 ppm initial sulfur. Commercial diesel supplied by Zawia Refinery contained 261 ppm sulfur initially. Tests used 15 mL diesel and activated bentonite, varying pH, temperature, contact time, and dose. Sulfur was measured by ED-XRF.

2.4 Calculations, equilibrium and kinetics

Sulfur removal and adsorption capacity were calculated from R (%) = [(C_0 − Ce)/C_0] × 100 and qe = [(C_0 − Ce)V]/m, where C_0 and Ce are initial and equilibrium concentrations, V is liquid volume and m is adsorbent mass. Langmuir and Freundlich equations were applied to equilibrium data. Thermodynamic parameters were calculated using the (van't Hoff) relationship, and pseudo-first- and pseudo-second-order models were used for kinetic analysis.[26-28]

2.5 Experimental design and statistics

A central composite response-surface design evaluated temperature (50–120 °C) and pH (5–9) for diesel sulfur removal using 13 runs. ANOVA was used to assess linear, quadratic and interaction terms; $p < 0.05$ was considered significant. The source thesis reports R^2 = 89.10% and a numerical optimum of 115.8 °C and pH 6.94 with predicted removal of 56.76%. Because lack-of-fit was also significant ($p = 0.003$), the model optimum is treated as a cautious model estimate rather than a validated operating point.

3. RESULTS AND DISCUSSION

3.1 Selection of activated bentonite

As shown in (Table 1), the 100 °C/5 M HCl-treated bentonite exhibited the best screening performance, achieving the lowest residual sulfur concentration (Ce = 608 ppm), the highest sulfur removal efficiency (R = 11.60%), and the highest adsorption capacity (qe = 1.20 mg/g). In comparison, raw clay showed only 0.58% sulfur removal and a qe of 0.06 mg/g. The results also indicate that increasing the HCl concentration from 5 to 10 M at 100 °C did not further improve sulfur removal, while increasing the treatment temperature to 200 °C resulted in lower removal efficiencies for both acid concentrations. Thus, the 100 °C/5 M HCl treatment provided the most favorable combination of treatment conditions among the materials investigated and was therefore selected for subsequent adsorption experiments. The increase in sulfur removal following acid treatment is consistent with changes in the adsorbent surface properties and partial leaching of mineral components, which may enhance the accessibility of adsorption sites.[8,15-19] However, confirmation of these mechanisms requires complementary characterization of the treated bentonite. Overall, the screening results (Table 1) support selecting the 100 °C/5 M HCl-treated bentonite for subsequent adsorption experiments.

Table1: Sulfur Removal by Activated Bentonite at 25 °C.

Adsorbent	Ce (ppm)	R (%)	qe (mg/g)
Raw clay	684	0.58	0.06
Washed clay	655	4.79	0.495
Thermal, 100 °C	640	6.97	0.72
Thermal, 200 °C	643	6.54	0.675
Chemical, 100 °C + 5 M HCl	608	11.60	1.20
Chemical, 100 °C + 10 M HCl	614	10.70	1.11
Chemical, 200 °C + 5 M HCl	626	9.00	0.93
Chemical, 200 °C + 10 M HCl	635	7.70	0.795

3.2 Structural and thermal characterization

The XRD patterns of the raw, heat-treated, and chemically treated bentonite samples (Fig. 1) exhibit the characteristic diffraction features of a layered smectite structure. Thermal treatment at 100 °C resulted in a reduction in the intensity and broadening of the low-angle basal reflection, which is consistent with dehydration and changes in the interlayer environment. The heat-treated sample exhibited a basal reflection at approximately 2θ = 7.84° (d = 11.26 Å), based on the peak positions obtained from the XRD data. Following chemical activation with 5 M HCl and subsequent heat treatment at 100 °C, the basal reflection shifted toward a lower diffraction angle, occurring at approximately 2θ = 5.71° (d = 15.46 Å), accompanied by increased broadening. This change in basal spacing may be associated with protonation, partial structural disorder, and acid-induced leaching of mineral components. The persistence of the reflection assigned to the 060 plane near 2θ ≈ 62.3° suggests that the basic dioctahedral character of the smectite framework was retained after treatment.[20-24]

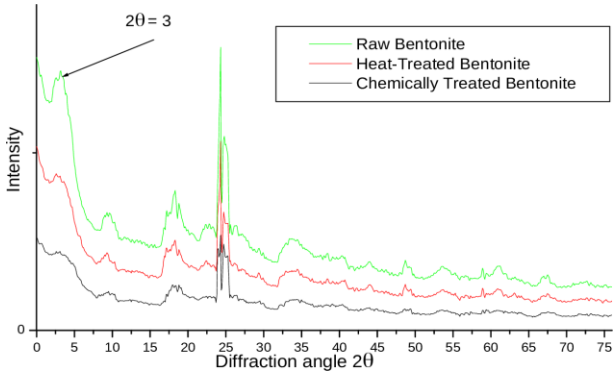


Fig. 1: XRD patterns of raw, heat-treated, and chemically treated bentonite.

Fig 2 displays the FTIR spectra of raw, thermally treated (100 °C), and acid-activated (5 M HCl + 100 °C) Libyan bentonite. The results, focusing on the main absorption bands at 3392 cm^{-1} (hydroxyl group stretching), 1580 cm^{-1} (H–O–H vibrations trapped in the deep clay layers), and 917 cm^{-1} (Si–O–Al or structural OH vibrations in montmorillonite), reveal clear variations among the samples.

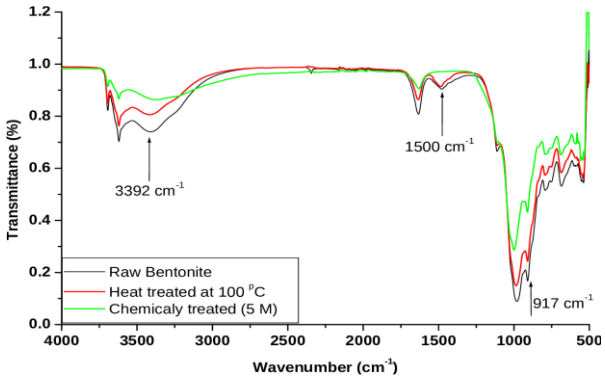


Fig. 2: FTIR spectra of raw, heat-treated and chemically treated bentonite.

The 3392 cm^{-1} peak was more intense in the raw and heat-treated samples, indicating partial loss of surface water. In the chemically treated sample, this peak was less intense, suggesting a chemical reaction of the OH groups. At the 1580 cm^{-1} region, the results for the raw and heat-treated samples were nearly identical, indicating similar water content, whereas the chemically treated sample exhibited a change in peak intensity, demonstrating that acid treatment affected the binding of water groups within the clay layers. For the 917 cm^{-1} peak, the chemically treated sample exhibits a less pronounced peak than the raw and heat-treated samples, indicating a structural modification resulting from the acid reaction with the clay components. Generally, heat treatment showed a negligible effect on the basic structure of bentonite. Chemical treatment enhanced clay porosity and adsorption capacity more effectively than heat activation alone.[21, 22]

TGA analysis (Fig. 3) showed greater weight loss for the raw and heat-treated samples than for the chemically treated sample, indicating higher water content in the raw sample, followed by the heat-treated and chemically treated samples.

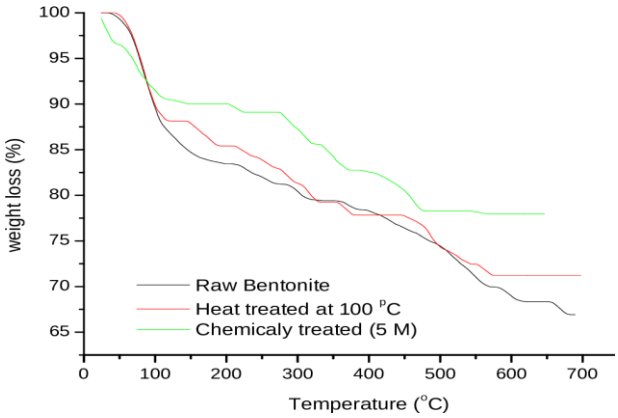


Fig. 3: TGA profiles of raw, heat-treated and chemically treated bentonite.

At a temperature from 150 to 400 °C, the mass loss increased, and this indicated the loss of hydroxyl groups in the deep layers. At temperatures above 400 to 700 °C, there was a similar weight loss for both the raw and heat-treated samples, and a greater weight loss than that of the chemically treated sample. This indicates that the acid extracted the expellable components by dissolving Al^{+3} and Mg^{+2}, reducing the organic mass and any biodegradable components, resulting in a final mass that is more resistant to thermal decomposition.[20-24]

3.3 Desulfurization of the model compound

At pH 7, increasing the temperature from 25 to 120 °C progressively enhanced thiophene removal from the model oil, as shown in (Table 2 and Fig. 4.) The sulfur removal efficiency increased from 25.6% at 25 °C to 94.0% at 120 °C, while the corresponding adsorption capacity (qeq_e) increased from 1.92 to 7.05 mg/g. The most pronounced improvement occurred between 25 and 80 °C, where the removal efficiency increased from 25.6% to 75.0%. Above 100 °C.

However. The improvement became less pronounced, with removal increasing only from 90.8% at 100 °C to 94.0% at 120 °C (Table 2; Fig. 4). This behavior indicates that higher temperature favored sulfur removal under the investigated experimental conditions, while the gradual leveling-off at the highest temperatures suggests that the adsorption system was approaching a limiting removal level.

Table2: Effect of Temperature on Thiophene Adsorption at pH 7.

T (°C)	Ce (ppm)	R (%)	qe (mg/g)
25	372	25.6	1.92
50	298	40.4	3.03
60	234	53.2	3.99
80	125	75.0	5.625
90	72	85.6	6.42
100	46	90.8	6.81
110	36	92.8	6.96
120	30	94.0	7.050

The enhanced removal at elevated temperature may be associated with improved mass transfer and greater accessibility of adsorption sites within the bentonite structure.

Nevertheless, these results alone do not establish the thermodynamic nature of the adsorption process; confirmation of whether the process is endothermic would require equilibrium measurements at multiple temperatures followed by determination of the corresponding thermodynamic parameters. The results therefore demonstrate a strong positive temperature effect on Thiophene removal from the model oil, with 120 °C giving the highest removal efficiency (94.0%) and adsorption capacity (7.05 mg/g) among the temperatures investigated (Table 2; Fig. 4).

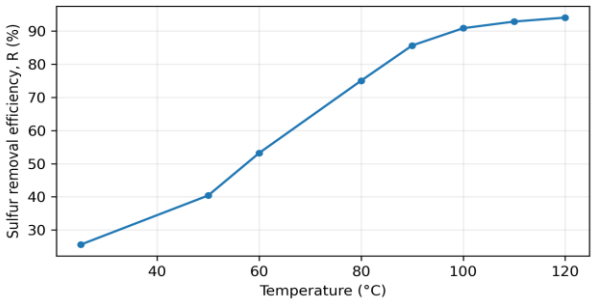


Fig. 4: Effect of temperature on sulfur removal from Thiophene model oil at pH 7.

At pH 7, increasing temperature from 25 to 120 °C increased removal from 25.6 to 94.0% and qe from 1.92 to 7.05 mg/g, indicating thermally favored adsorption in the model system. The reported pH comparison also showed pH 7 to be superior to pH 5 and 9. Contact-time experiments gave the maximum reported removal at 60 min, while increasing initial sulfur concentration from 100 to 500 ppm decreased percentage removal from 98.9 to 94.0% but increased qe from 1.4835 to 7.05 mg/g.

3.4 Desulfurization of commercial diesel

The desulfurization behavior of commercial diesel was evaluated by examining the effects of pH, temperature, adsorbent dose, and contact time under one-factor-at-a-time experimental conditions. As shown in (Table 3), the effect of pH was relatively modest at 120 °C, with sulfur removal efficiencies of 48.2, 50.9, and 45.2% at pH 5, 7, and 9, respectively. The highest removal was obtained at pH 7, corresponding to a residual sulfur concentration (CeCe) of 128 ppm and an adsorption capacity (qeq_e) of 1.995 mg/g. Accordingly, pH 7 was selected for the subsequent experiments.

Table3: Effect of pH on commercial diesel at 120 °C, 1 g adsorbent and 60 min.

pH	Ce (ppm)	R (%)	qe (mg/g)
5	135	48.2	1.890
7	128	50.9	1.995
9	143	45.2	1.770

The temperature response of commercial diesel differed substantially from that observed for the thiophene model oil. As shown in (Fig. 5), sulfur removal increased from 15.7% at 25 °C to a maximum of 57.0% at 80 °C, followed by a decrease to 47.8% at 100 °C and relatively stable removal of approximately 49–51% at 110–120 °C. This non-monotonic response indicates that increasing temperature did not continuously enhance sulfur removal in the real-fuel system. The difference from the model-oil behavior may reflect the greater.

Complexity of commercial diesel, which contains multiple sulfur-containing compounds and other hydrocarbons that can compete for adsorption sites and influence mass transfer. Therefore, the temperature effect observed for the simplified

thiophene model system cannot be directly extrapolated to commercial diesel.

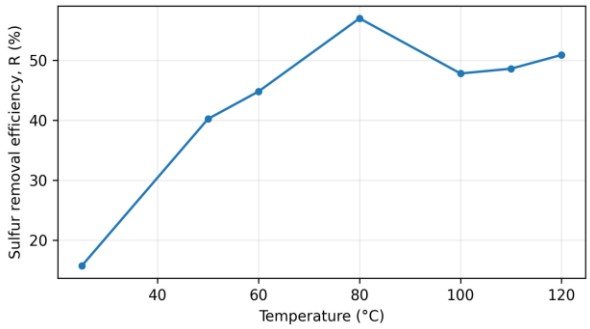


Fig. 5: Temperature effect on sulfur removal from commercial diesel at pH 7.

The effect of adsorbent dose was investigated at 80 °C and pH 7. As shown in (Fig. 6 and Table 4), increasing the adsorbent dose from 1.00 to 2.00 g progressively increased sulfur removal from 57.00 to 70.49%, while the residual sulfur concentration decreased from 112 to 77 ppm. In contrast, (qe) decreased from 2.235 to 1.380 mg/g as the adsorbent dose increased. This decrease in adsorption capacity per unit mass is expected because the same sulfur inventory was distributed over an increasing mass of adsorbent, resulting in a lower average sulfur loading despite the higher overall removal efficiency. These results demonstrate that increasing the adsorbent dose improved the overall sulfur removal but reduced the adsorption capacity expressed per gram of adsorbent.

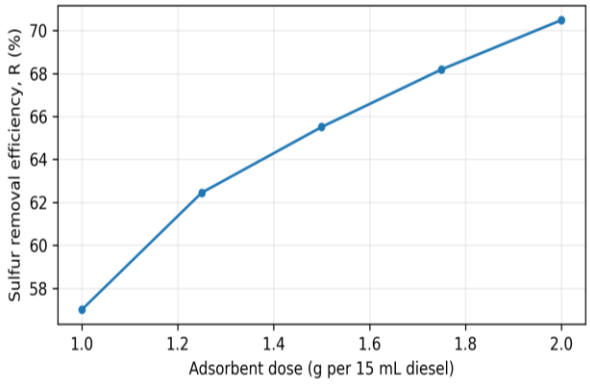


Fig. 6: Effect of adsorbent dose on commercial diesel at 80 °C and pH 7.

Table4: Adsorbent-dose effect on commercial diesel at 80 °C and pH 7.

Dose (g)	Ce (ppm)	R (%)	qe (mg/g)
1.00	112	57.00	2.235
1.25	98	62.45	1.956
1.50	90	65.51	1.710
1.75	83	68.19	1.525
2.00	77	70.49	1.380

The effect of contact time was subsequently evaluated at 80 °C, pH 7, and an adsorbent dose of 2 g. As shown in (Table 5), sulfur removal increased from 59.0% at 30 min to a maximum of 70.49% at 60 min, followed by a decrease to 66.66% and 64.75% at 90 and 120 min, respectively. Thus, the highest removal was obtained after 60 min, suggesting that this contact period provided the most favorable removal under the investigated conditions. The subsequent decrease in removal at longer contact times may be associated with changes in adsorption equilibrium or redistribution/desorption of weakly retained sulfur species. However, confirmation of these mechanisms would require additional kinetic and equilibrium analysis.

Table 5: Contact-time effect on commercial diesel at 80 °C, pH 7 and 2 g adsorbent.

Time (min)	Ce (ppm)	R (%)	qe (mg/g)
30	107	59.0	1.134
60	77	70.49	1.380
90	87	66.66	1.305
120	92	64.75	1.267

Overall, among the one-factor experimental conditions investigated for commercial diesel, the highest observed sulfur removal was 70.49% at 80 °C, pH 7, an adsorbent dose of 2.00 g, and a contact time of 60 min, as indicated by (Tables 4 and 5). Under these conditions, the residual sulfur concentration was 77 ppm and the corresponding adsorption capacity was 1.380 mg/g. These conditions therefore provided the highest experimental removal observed in the present one-factor screening experiments; however, they should not be considered statistically optimized operating conditions unless confirmed through a multivariable optimization approach.

3.5 RSM and ANOVA

A central composite design (CCD) was used to evaluate the effects of temperature and pH on sulfur removal from commercial diesel. As shown in (Table 6), sulfur removal ranged from 30.6 to 57.0%, with the highest measured removal of 57.0% occurring at 85 °C and pH 7. The repeated center-point runs showed relatively similar responses, although some experimental variability was observed.

Table 6: Central composite response-surface design and measured diesel sulfur-removal response.

Run	T (°C)	pH	R (%)
1	50	5	30.6
2	85	7	54.5
3	50	9	32.0
4	120	5	48.2
5	85	7	54.5
6	85	7	56.0
7	85	7	55.0
8	120	9	45.2
9	85	5	35.0
10	85	9	38.0
11	120	7	50.9
12	50	7	40.0
13	85	7	57.0

The ANOVA results (Table 7) showed that the overall model was statistically significant ($F=11.45$, $p=0.003$). Temperature had a significant linear effect on sulfur removal ($F=16.47$, $p=0.005$), whereas the linear effect of pH was not significant ($p=0.895$). However, the quadratic pH term was highly significant ($F=26.08$, $p=0.001$), indicating a nonlinear pH response. The temperature-squared and temperature × pH interaction terms were not significant ($p=0.163$ and $p=0.616$, respectively).

These trends are illustrated in (Fig. 7), where sulfur removal increased with temperature and exhibited a maximum response near pH 7. The response-surface contour (Fig. 8) similarly indicates a high-response region at elevated temperatures and near-neutral pH.

Table7: ANOVA for the diesel response-surface model.

Source	DF	Adj SS	Adj MS	F	P
Model	5	1006.90	201.379	11.45	0.003
Linear	2	290.14	145.071	8.25	0.014
Temperature	1	289.81	289.815	16.47	0.005
pH	1	0.33	0.327	0.02	0.895
Temperature²	1	42.87	42.867	2.44	0.163
pH²	1	458.87	458.872	26.08	0.001
T×pH	1	4.84	4.840	0.28	0.616
Lack-of-fit	3	118.46	39.487	33.61	0.003
Pure error	4	4.70	1.175	—	—
Total	12	1130.06	—	—	—

However, the significant lack-of-fit ($F=33.61$, $p=0.003$; (Table 7) indicates that the quadratic model does not fully capture the experimental variability. Therefore, the region identified in (Fig. 8) should be regarded as a high-response region rather than a statistically validated optimum. Overall, the RSM results identify temperature as the main linear factor and pH as an important nonlinear factor governing sulfur removal under the investigated conditions.

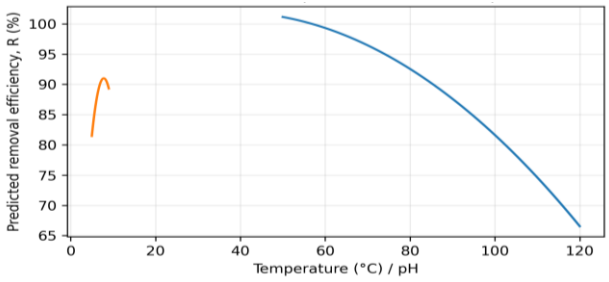


Fig. 7: Main-effects visualization generated from the regression equation reported in the thesis.

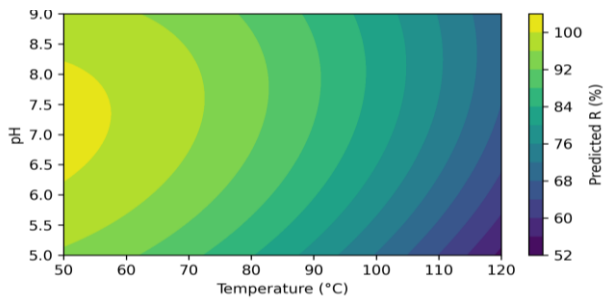


Fig. 8: Response-surface contour generated from the regression equation reported in the thesis.

3.6 Model compound versus real diesel

The desulfurization performance of the thiophene model compound and commercial diesel was compared under the same operating conditions of 80 °C, pH 7, 1 g adsorbent, and 15 mL solution, as presented in (Table 8). At 60 min, the model compound achieved 75.0% sulfur removal, compared with 57.0% for commercial diesel, indicating a substantially higher removal efficiency for the simplified model system. At 30 min, however, the removal efficiencies were very similar (46.4% for the model compound and 46.3% for real diesel), while the subsequent contact times showed greater differences between the two systems (Table 8).

Table 8: Comparison of model compound and real diesel under identical conditions (80 °C, pH 7, 1 g, 15 mL).

Time (min)	RD Ce	RD R (%)	MC Ce	MC R (%)
30	140	46.3	286	46.4
60	112	57.0	125	75.0
90	124	52.4	234	53.2
120	120	54.0	217	56.6

The lower and less consistent removal observed for commercial diesel may be attributed to its more complex matrix, in which different sulfur-containing compounds and hydrocarbon components can compete for adsorption sites and affect mass transfer and adsorbent–solute interactions. Thus, the thiophene model compound provides a useful simplified system for evaluating adsorption behavior, but its performance should not be directly extrapolated to commercial diesel. The comparison in (Table 8) therefore demonstrates the importance of validating the adsorption process using the actual fuel matrix.

3.7 Adsorption isotherms

The adsorption isotherms of sulfur compounds were evaluated using the Langmuir and Freundlich models for both the model compound and commercial diesel. As shown in Table 9.

Table 9: Isotherm parameters for the model compound.

Model compound	Model	qmax	KL	R^2
	Langmuir	8.487	0.1603	0.9956
	Freundlich	—	—	0.9869

The model compound exhibited a higher coefficient of determination for the Langmuir model (R2=0.9956R^2=0.9956) than for the Freundlich model (R2=0.9869R^2=0.9869), indicating that the Langmuir model provided the better fit to the experimental data.

For commercial diesel, the Freundlich model provided a substantially better fit (R2=0.991R^2=0.991) than the Langmuir model (R2=0.842R^2=0.842), as reported in (Table 9). The Freundlich exponent (n=0.77n=0.77) indicates a non-ideal adsorption behavior and suggests that the heterogeneous fuel matrix does not conform well to the assumptions of monolayer adsorption on energetically equivalent sites. The comparatively poor Langmuir fit further supports the presence of heterogeneous adsorption behavior in the real diesel system. Overall, the isotherm analysis indicates that adsorption behavior differs between the simplified model compound and commercial diesel, with the former being better described by the Langmuir model and the latter by the Freundlich model.

The adsorption behavior of sulfur compounds in commercial diesel was evaluated using the Langmuir and Freundlich isotherm models. As shown in (Table 10), the Freundlich model provided a substantially better fit to the experimental data (R2=0.991R^2=0.991) than the Langmuir model (R2=0.842R^2=0.842). The Freundlich constants were Kf=0.0048K_f=0.0048 and n=0.77n=0.77, indicating that the adsorption behavior is better described by a heterogeneous surface model. The comparatively lower Langmuir fit and the absence of physically meaningful Langmuir parameters further support this interpretation. The corresponding isotherm plots shown in (Figs. 9 and 10) illustrate the different linearized fits, with the Freundlich relationship providing the more consistent representation of the experimental behavior. Overall, the results indicate that sulfur adsorption from commercial diesel is predominantly heterogeneous and is better represented by the Freundlich model (Table 10; Figs. 9 and 10).

Table 10: Isotherm parameters for commercial diesel.

Real diesel	Model	R^2	Kf	n
	Langmuir	0.842	non-physical	—
	Freundlich	0.991	0.0048	0.77

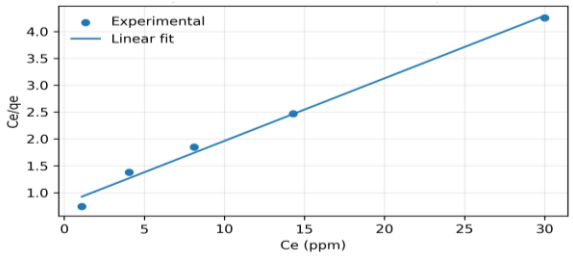


Fig. 9: Langmuir linearization for sulfur adsorption from the model compound.

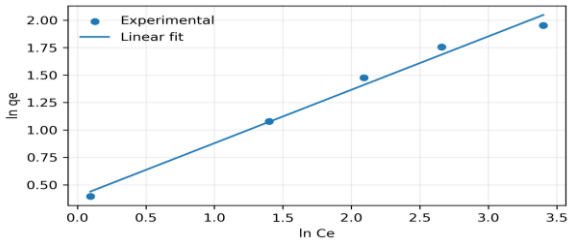


Fig. 10: Freundlich linearization for sulfur adsorption from the model compound.

3.8 Thermodynamics and kinetics

The thermodynamic parameters for sulfur adsorption are summarized in(Table 11). For the model compound, the positive ΔH∘\Delta H^\circ value (+49.97 kJ/mol) indicates an endothermic process, while ΔG∘\Delta G^\circ decreased from +12.32 to +4.735 kJ/mol as temperature increased, indicating that the process became more favorable at higher temperature. Commercial diesel showed a similar trend, with ΔH∘=+31.5\Delta H^\circ=+31.5 kJ/mol and ΔG∘\Delta G^\circ decreasing from +14.57 to +11.49 kJ/mol (Table 11). The positive ΔG∘\Delta G^\circ values indicate that adsorption was not spontaneous under the investigated conditions, although increasing temperature reduced the thermodynamic barrier to adsorption.

Table 11: Thermodynamic parameters reported in the thesis.

System	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)	ΔG° range (kJ/mol)
Model compound	+49.97	+0.1165	+12.32 to +4.735
Real diesel	+31.5	+0.0575	+14.57 to +11.49

The kinetic results are presented in (Table 12). For the model compound, the pseudo-second-order (PSO) model provided a better fit (\(R^2=0.97\)) than the pseudo-first-order (PFO) model (\(R^2=0.58\)), with a theoretical capacity of 6.19 mg/g compared with the experimental value of 7.05 mg/g. For commercial diesel, both models showed high \(R^2\) values, although the PSO model gave a theoretical capacity (2.18 mg/g) closer to the experimental value (2.235 mg/g).

Table 12: Kinetic parameters for sulfur adsorption on activated bentonite.

System	Model	qe,exp	qe,theor	R^2	k
Model compound	PFO	7.05	2.81	0.58	0.0081
Model compound	PSO	7.05	6.19	0.97	0.0432
Real diesel	PFO	2.235	1.57	0.999	0.0139
Real diesel	PSO	2.235	2.18	0.992	0.133

The corresponding PSO linearizations are shown in Figs. 11 and 12. Overall, the kinetic results indicate that the PSO model provides a closer representation of the adsorption data, particularly when the theoretical and experimental capacities are considered together (Table 12; Figs. 11 and 12). However, a better PSO fit alone does not establish chemisorption; the adsorption mechanism should be interpreted in conjunction with the thermodynamic and spectroscopic evidence.[27,28]

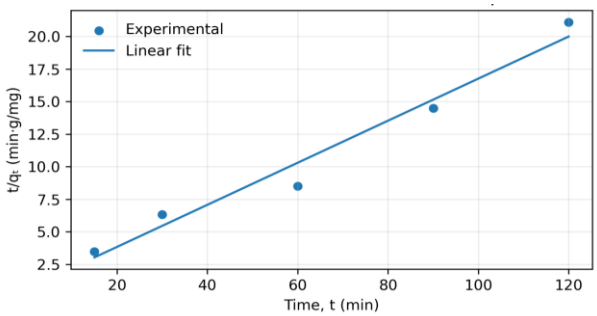


Fig. 11: Pseudo-second-order kinetic linearization for sulfur adsorption from the model compound.

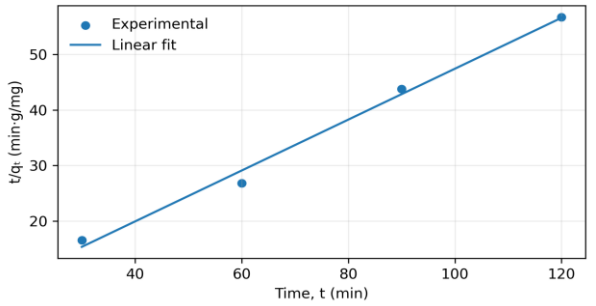


Fig. 12: Pseudo-second-order kinetic linearization for sulfur adsorption from commercial diesel.

4. CONCLUSION

Hydrochloric acid activation improved the sulfur-removal performance of Libyan bentonite,

with the 100 °C/5 M HCl treatment identified as the most effective material during adsorbent screening. In the thiophene model oil, sulfur removal increased with temperature and reached 94.0% at 120 °C and pH 7, with an adsorption capacity of 7.05 mg/g. For commercial diesel, the highest removal observed under the one-factor-at-a-time experiments was 70.49% at 80 °C, pH 7, 2 g adsorbent, and 60 min.

The isotherm results showed that the model compound was better described by the Langmuir model, whereas commercial diesel was better represented by the Freundlich model, reflecting the more heterogeneous nature of the real-fuel matrix. Thermodynamic analysis indicated an endothermic and non-spontaneous adsorption process under the investigated conditions, while the pseudo-second-order model provided a better overall kinetic description, although this does not by itself establish a chemisorption mechanism.

The RSM analysis identified temperature as the principal linear factor and pH as a significant nonlinear factor. However, the significant lack-of-fit indicates that the fitted model should not be used to claim a statistically validated optimum. Overall, the results demonstrate the potential of acid-activated Libyan bentonite for sulfur reduction in both model and real fuel systems. Further work should focus on adsorbent regeneration, continuous-flow operation, sulfur-species selectivity, adsorbent consumption, process stability, and economic feasibility before practical or industrial application can be assessed.

AUTHOR CONTRIBUTIONS

All authors contributed equally for: Conceptualization, methodology, writing – original draft, investigation, data curation, validation, manuscript preparation, critical review, writing – review & editing, and final approval of the manuscript.

CONFLICT OF INTEREST

The authors declare no conflicts of interest concerning the research, authorship, and publication of this article.

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