

RESEARCH PAPER

Synthesis of a ZnO/Nanobiochar Nanocomposite Derived from Wheat Husk and its Application for the Adsorptive Removal of Sulfur Compounds from Iraqi Crude Oil

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ARTICLE INFO

Article History:

Received 21 May 2026

Accepted 18 July 2026

Published 01 October 2026

Keywords:

Adsorptive desulfurization

Iraqi crude oil

Nanobiochar

Pseudo-second-order kinetics

ZnO nanoparticles

ABSTRACT

The presence of organosulfur compounds in crude oil remains one of the most persistent problems facing the petroleum industry, since these species contribute to environmental pollution and complicate downstream refining. In the present study, a low-cost ZnO/nanobiochar (ZnO/NBC) composite was synthesized from wheat husk, with the aim of producing an effective adsorbent for the desulfurization of Iraqi crude oil. Wheat-husk biochar was first prepared by pyrolysis at 700 °C for 5 h, and then converted into nanobiochar through treatment with concentrated nitric acid (68 %). Zinc oxide nanoparticles were synthesized by a simple precipitation–calcination route, and loaded onto the nanobiochar via an ultrasonic-assisted procedure in ethanol. The as-prepared materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM) with particle-size analysis, and energy-dispersive X-ray spectroscopy (EDS). The XRD pattern of the composite confirmed the coexistence of a hexagonal wurtzite ZnO phase together with the carbon backbone of the biochar, while FESEM and TEM showed a fairly uniform dispersion of ZnO nanoparticles on the carbon matrix with a mean particle size of about 49 nm. Batch desulfurization experiments were carried out on a model oil prepared from Iraqi crude oil and n-hexane (3:1 v/v) with an initial sulfur content of 4.7 wt %. The composite achieved a sulfur-removal efficiency of 76.38 % at 333 K, 70 min, and 0.5 g of adsorbent. The kinetic data were best described by a pseudo-second-order model ($R^2 = 0.999$), while the thermodynamic analysis indicated that the process was endothermic ($\Delta H^\circ = +36.8 \text{ kJ mol}^{-1}$) and became spontaneous at elevated temperatures.

How to cite this article

Abdullah I., Al khazraji A. Synthesis of a ZnO/Nanobiochar Nanocomposite Derived from Wheat Husk and its Application for the Adsorptive Removal of Sulfur Compounds from Iraqi Crude Oil. J Nanostruct, 2026; 16(4):4781-4791. DOI: 10.22052/JNS.2026.04.027

INTRODUCTION

Iraqi crude oil is well known for its relatively high sulfur content, which often exceeds the limits suggested by international refining standards. Sulfur-containing molecules — mostly thiophenes, benzothiophenes and dibenzothiophenes — pose

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serious environmental and economic concerns since they release SO_x during combustion and cause deactivation of refining catalysts [1, 2]. Conventional hydrodesulfurization (HDS) is still the most widely used technology, but it requires high pressures, expensive catalysts and elevated



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temperatures, in addition to its limited efficiency against bulky aromatic sulfur species [3]. For these reasons, alternative approaches such as oxidative, biological, extractive and adsorptive desulfurization have attracted growing attention in recent years [4, 5].

Among these, adsorptive desulfurization (ADS) is particularly interesting due to the moderate operating conditions, the low energy consumption and the feasibility of developing selective adsorbents from cheap precursors [6]. Biochar made from agricultural leftovers is one of the most promising materials for this purpose: it has a high carbon content, a tuneable surface chemistry and can be easily activated to get nanostructured forms with increased surface area [7, 8]. In particular, wheat husk is a plentiful by-product of Iraqi agricultural operations and converting it to nanobiochar is a green way to valorise this waste.

The performance of carbonaceous adsorbents can be further increased by hybridisation with metal oxide nanoparticles. Zinc oxide (ZnO) is a low toxicity n-type semiconductor with a strong affinity towards sulphur lone pairs, making it suited to bind thiophenic chemicals [9, 10]. Loading ZnO nanoparticles on a carbon support is known to suppress particle aggregation and to combine the high adsorption capacity of biochar with the chemical reactivity of the oxide [11]. In light of the above, the present work aimed to prepare a ZnO/nanobiochar composite using wheat husk as the biomass source, to characterize the obtained material by XRD, TEM, FESEM and EDS, and to

evaluate its performance for the removal of sulfur compounds from Iraqi crude oil. The effects of contact time, temperature and adsorbent dose are examined, and the kinetics, equilibrium and thermodynamics of the process are discussed in detail.

MATERIALS AND METHODS

Chemicals and crude oil

Wheat husks were collected from agricultural farms in Diyala Governorate (Iraq). Concentrated nitric acid (HNO_3 , 68 %), zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], sodium hydroxide (NaOH), ethanol (99 %) and n-hexane were all of analytical grade and used as received. Distilled and deionized water was used throughout the work. Iraqi crude oil samples were provided by a local refinery and stored in a sealed glass container until used.

Preparation of nanobiochar (NBC) from wheat husk

The collected husks were properly cleaned with distilled water to remove dust and clinging contaminants, dried at room temperature in absence of direct sunlight and crushed in a domestic electric grinder to get fine and uniform powder. A simple heating source was used to execute the pre-carbonization phase to eliminate the volatile materials and lower the organic content. The samples were then placed in a pyrolysis furnace and heated to 700 °C for 5 h under limited-oxygen conditions. The resultant biochar was cooled to room temperature and then

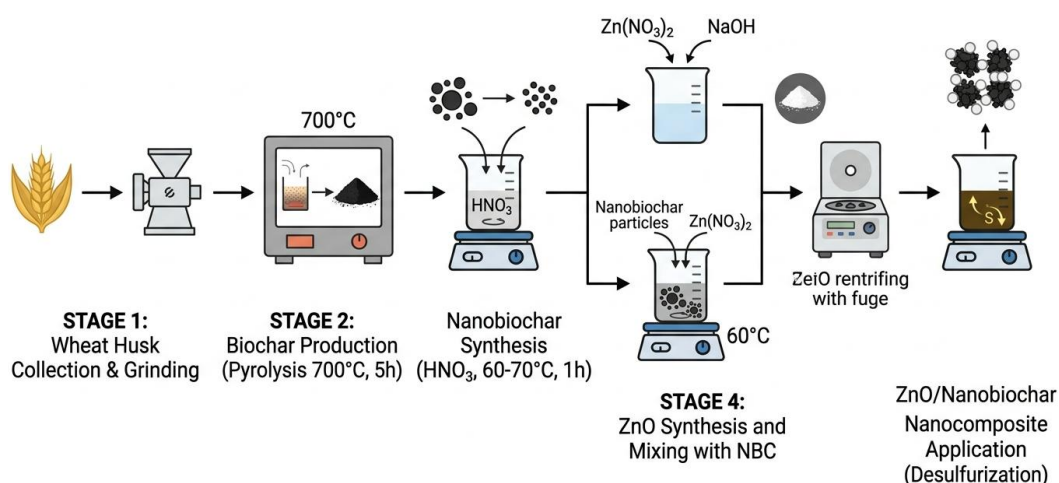


Fig. 1. Schematic representation of the synthesis route of the ZnO/nanobiochar nanocomposite from wheat husk and its application for the adsorptive removal of sulfur compounds from Iraqi crude oil.

processed again into a fine powder [12].

To convert the biochar into nanobiochar, 1.0 g of wheat-husk biochar was dispersed in 10 mL of deionized water, and the suspension was titrated with a solution of concentrated HNO_3 (6 mL of 68 % HNO_3 diluted in 80 mL of deionized water). The mixture was heated at 60–70 °C for 1 h under continuous magnetic stirring. The resulting nanobiochar was washed several times with deionized water to remove residual acid, then dried for further use.

Synthesis of ZnO nanoparticles

ZnO nanoparticles were prepared by a simple co-precipitation procedure. In brief, 0.6 g of NaOH was dissolved in 50 mL of deionized water and the resulting solution was added dropwise into a $\text{Zn}(\text{NO}_3)_2$ solution (suitable amount in 50 mL deionized water) under continuous magnetic stirring. The white precipitate that formed was filtered, washed several times with deionized water until a near-neutral pH was obtained, and then dried. The dried hydroxide was finally calcined at 600 °C for 5 h to yield the ZnO nanoparticles.

Preparation of the ZnO/nanobiochar composite

One gram of wheat-husk nanobiochar was dispersed in 20 mL of 99 % ethanol, and 0.5 g of the prepared ZnO nanoparticles was dispersed in another 20 mL of 99 % ethanol. The two suspensions were mixed and sonicated in an ultrasonic bath for 30 min at 50 °C. After sonication, the mixture was kept under mechanical stirring at 55 °C for 3 h in order to ensure a homogeneous distribution of ZnO over the carbon support. The final composite was dried in an oven at 80 °C and stored in a dry container prior to use.

Characterization

The crystallinity and phase composition of the prepared materials were investigated by X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 10–80°. The average crystallite size (D) was estimated using the Debye–Scherrer equation:

$$D = K\lambda / (\beta \cos \theta)$$

where K is the shape factor (~ 0.9), λ is the X-ray wavelength, β is the entire width at half maximum of the peak in radians and θ is the Bragg angle. The surface morphology and particle-size distribution

were observed by field-emission scanning electron microscopy (FESEM, ZEISS) at 15 kV. No less than 95 particles were counted for each sample to plot the size histogram. Transmission electron microscopy (TEM, 100 kV) was used for additional investigation of the interior microstructure. The elemental composition was measured by Energy Dispersive X-ray Spectroscopy (EDS) connected to the FESEM.

Adsorption experiments

A model oil was prepared by mixing 75 mL of Iraqi crude oil with 25 mL of n-hexane (3:1 v/v); the mixture was stirred for 1 h before use in order to ensure full homogeneity. The initial sulfur content of the model oil was 4.7 wt %, measured using a standard sulfur analyzer. Batch experiments were carried out by mixing the model oil with a known mass of the ZnO/NBC composite in a glass flask under continuous magnetic stirring. After the desired contact time, the adsorbent was separated from the liquid phase by filtration and the residual sulfur content was measured. The sulfur removal efficiency (R %) and the adsorption capacity (q_t) were calculated using:

$$R(\%) = (C_0 - C_t) / C_0 \times 100$$

$$q_t = (C_0 - C_t) V / W$$

where C_0 and C_t are the initial and the residual sulfur concentrations, V is the volume of the model oil and W is the mass of the adsorbent. The effects of contact time (10–70 min), temperature (298, 313 and 333 K) and adsorbent dose (0.1–0.5 g) were examined while keeping the other parameters fixed. Each experiment was performed in duplicate, and the average value was reported.

RESULTS AND DISCUSSION

Characterization of the prepared materials

The structural, morphological and elemental content of the produced materials were characterised by XRD, TEM, FESEM and EDS, and the results are summarised in Figs. 2–5 and Tables 1 and 2. The XRD pattern of wheat-husk nanobiochar (Fig. 2) showed a broad reflection at a position of around $2\theta \approx 21.98^\circ$ and some less intense peaks, indicating a partly disordered carbon structure with some crystalline silicate residues typical for plant-derived biochar [13]. The average crystallite size was calculated using

the Scherrer equation based on the most intense peak position, resulting in a value of around 28.15 nm. The diffractogram of the synthesised ZnO was in good agreement with the standard hexagonal wurtzite phase (JCPDS card no. 36-1451) and characteristic reflections at $2\theta \approx 32.20^\circ$ (100), 34.86° (002), 36.69° (101), 47.96° (102), 56.99° (110), 63.25° (103), 66.76° (200), 68.31° (112) and 69.44° (201) were clearly observed [14]. The most

intense peak corresponded to the (101) plane ($d \approx 2.45 \text{ \AA}$) and the average crystallite size was 33.94 nm. The main ZnO reflections were basically kept in the composite, with the (101) peak at 36.60° ($d \approx 2.46 \text{ \AA}$) proving that the wurtzite phase of the oxide was preserved during the loading procedure, and a broad feature at around 22.20° indicating the presence of the carbon support under the oxide. There was no additional phase or impurity

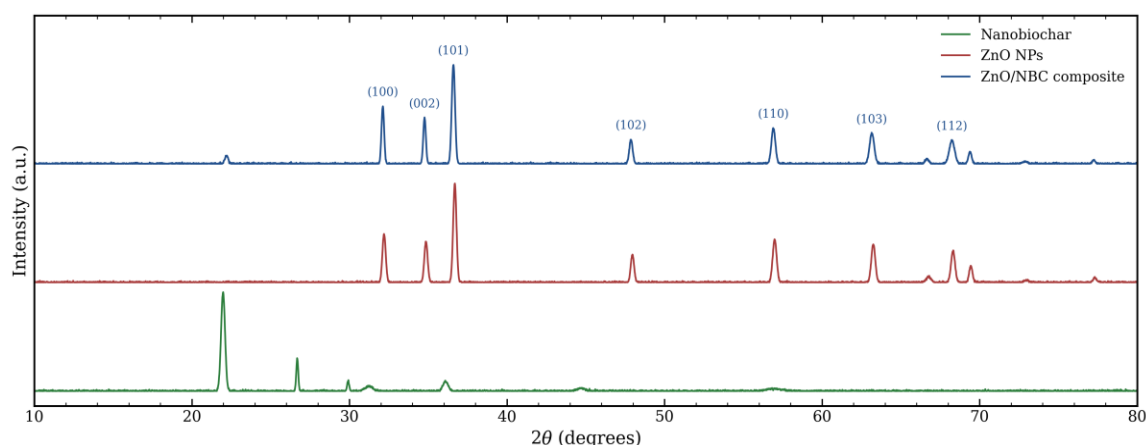


Fig. 2. XRD patterns of the wheat-husk nanobiochar, the synthesized ZnO nanoparticles, and the ZnO/NBC composite.

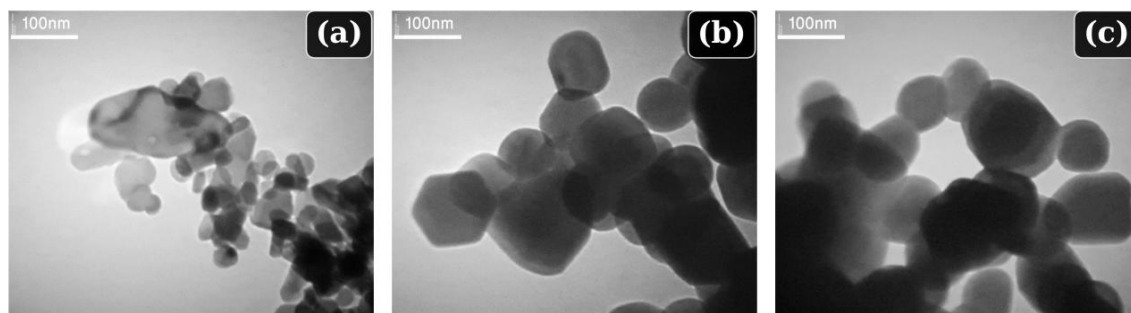


Fig. 3. TEM images of the prepared materials: (a) ZnO NPs; (b) wheat-husk nanobiochar; (c) ZnO/NBC composite.

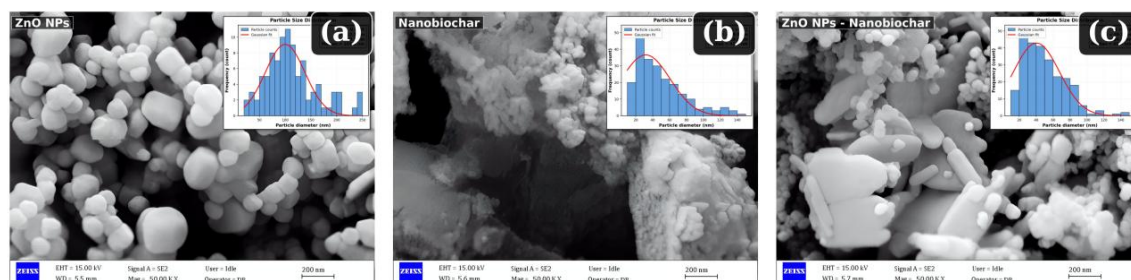


Fig. 4. FESEM images with particle-size histograms of the prepared materials: (a) ZnO NPs; (b) wheat-husk nanobiochar; (c) ZnO/NBC composite.

peak detected. The average crystallite size of the composite (33.9 nm) was almost the same as that of pure ZnO, implying that the carbon framework hindered the formation of new crystallites while not significantly affecting the ones already formed. These findings are consistent with the previously reported ZnO/biochar systems where the metal oxide remains the major crystalline phase and the biochar acts primarily as a porous scaffold [15, 16]. Further information about the internal microstructure was provided by TEM analysis (Fig. 3). The image of pristine ZnO (Fig. 3a) showed mainly spheroidal and polyhedral particles with sizes of about 30–100 nm and a few larger flat plate-like crystals, the dark contrast of some particles indicating high crystallinity, while the smaller surrounding grains showed that the precipitation–calcination route yields a population of crystallites which is not perfectly uniform — a behaviour often observed for ZnO prepared in the absence of surfactants. The wheat-husk

nanobiochar (Fig. 3b) reveals well-resolved polygonal nanostructures with smooth edges, with sizes in the range of approximately 80 to 200 nm. The presence of well-defined hexagonal contours, together with more rounded carbon clusters, suggests that crystalline silicate residues originally present in the plant tissues of the wheat husk are embedded within the carbonaceous matrix, consistent with the XRD reflection at $2\theta \approx 21.98^\circ$ and the high oxygen content obtained by EDS. In the case of the ZnO/NBC composite (Fig. 3c), the TEM image displayed a high density of darker, polyhedral particles attached to and intermingled with lighter, more diffuse regions due to the carbon support; the particle boundaries were less sharp than for pristine ZnO, indicating an intimate contact between the oxide and the carbon framework rather than just a physical mixture, which is known to enhance both the dispersion of active sites and the electronic communication between the two phases, a feature often reported

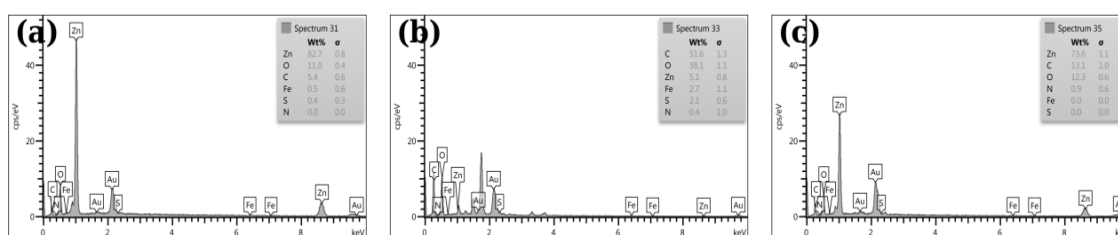


Fig. 5. EDS spectra of the prepared materials: (a) ZnO NPs; (b) wheat-husk nanobiochar; (c) ZnO/NBC composite.

Table 1. Main XRD reflections and crystallite sizes (D) of the ZnO/NBC composite, calculated from the Scherrer equation.

No.	2θ ($^\circ$)	d-spacing ($\text{\AA}$)	FWHM ($^\circ$)	Rel. Int. (%)	(hkl)	D (nm)
1	22.20	4.005	0.246	8.21	C (002)	33.21
2	32.12	2.787	0.197	57.98	ZnO (100)	42.07
3	34.77	2.580	0.197	46.23	ZnO (002)	42.30
4	36.60	2.455	0.246	100.00	ZnO (101)	34.11
5	47.87	1.900	0.246	24.56	ZnO (102)	35.30
6	56.91	1.618	0.295	35.95	ZnO (110)	30.66
7	63.16	1.472	0.344	30.63	ZnO (103)	26.91
8	68.24	1.374	0.394	23.63	ZnO (112)	24.39
9	69.39	1.354	0.246	11.99	ZnO (201)	39.25

Table 2. Elemental composition (wt %) of the ZnO NPs, nanobiochar and ZnO/NBC composite as determined by EDS (Au signal from conductive coating omitted).

Element	ZnO NPs (wt %)	Nanobiochar (wt %)	ZnO/NBC composite (wt %)
Zn	82.7	5.1	73.6
O	11.0	38.1	12.3
C	5.4	51.6	13.1
N	0.0	0.4	0.9
Fe	0.5	2.7	0.0
S	0.4	2.1	0.0

to improve the adsorption performance in carbon-supported metal oxide systems [16]. The surface morphology and particle-size distribution were further examined by FESEM (Fig. 4): the image of ZnO NPs (Fig. 4a) showed aggregated polyhedral particles with a mean diameter of 112.7 ± 50.1 nm (median ≈ 103.8 nm) and a certain degree of agglomeration that is commonly observed for ZnO synthesized by precipitation because of the high surface energy of the nanocrystals [17]; the nanobiochar (Fig. 4b) exhibited a rough, porous surface of small clusters with a mean diameter of 49.0 ± 29.0 nm (median ≈ 41.4 nm), and cavities and irregular pores were visible across the surface, consistent with the mesoporosity developed during pyrolysis and the subsequent acid treatment. In the composite (Fig. 4c) the ZnO nanocrystals were found to be dispersed over the carbon matrix, with the mean particle size calculated to be 49.2 ± 24.4 nm (median ≈ 45.4 nm). The standard deviation was significantly decreased (24.4 vs. 50.1 nm) compared to pristine ZnO, suggesting that the nanobiochar acts as a dispersing support, preventing aggregation and resulting in a more homogeneous distribution of the nanoparticles, a feature that is generally correlated with a higher density of accessible adsorption sites and hence better performance [18]. Elemental composition data from EDS (Fig. 5) confirmed the chemical purity of the three samples: the ZnO sample (Fig. 5a) was dominated by Zn (82.7 wt %) and O (11.0 wt %), with small amounts of C (5.4 wt %) and traces of Fe and S, the Au signal originating from the conductive coating applied before imaging; the nanobiochar (Fig. 5b) gave C (51.6 wt %) and O (38.1 wt %) as main

elements together with traces of Zn, Fe, S and N, consistent with the carbonaceous backbone of plant biomass [19]; and the composite (Fig. 5c) showed Zn (73.6 wt %), C (13.1 wt %), O (12.3 wt %) and a small amount of N (0.9 wt %), where the residual S signal present in the bare biochar dropped almost to zero, suggesting that sulfur-containing surface groups had reacted with or were effectively covered by the ZnO phase, while the coexistence of Zn–O and C signals further supports the successful formation of the hybrid material.

Adsorptive desulfurization experiments

Effect of contact time

The influence of contact time on the desulfurization efficiency was examined in the range 10–70 min, at 298 K with an adsorbent dose of 0.5 g (Fig. 6a). The sulfur-removal percentage gradually increased from about 1.3 % at 10 min up to 46.2 % at 70 min, although the rate of removal was clearly highest during the first 40 min. This kind of trend is typical for adsorbent–adsorbate systems in which a large number of unoccupied sites are initially available, leading to a fast uptake at the start of the experiment; afterwards, the remaining sites become harder to access because of repulsion between adsorbed and free sulfur molecules and partial blocking of pores [20]. Even though equilibrium was not yet fully reached at 70 min, the rate of change had clearly slowed down, and 70 min was therefore selected as the operating contact time for the subsequent experiments.

Effect of temperature

The effect of temperature was studied at 298,

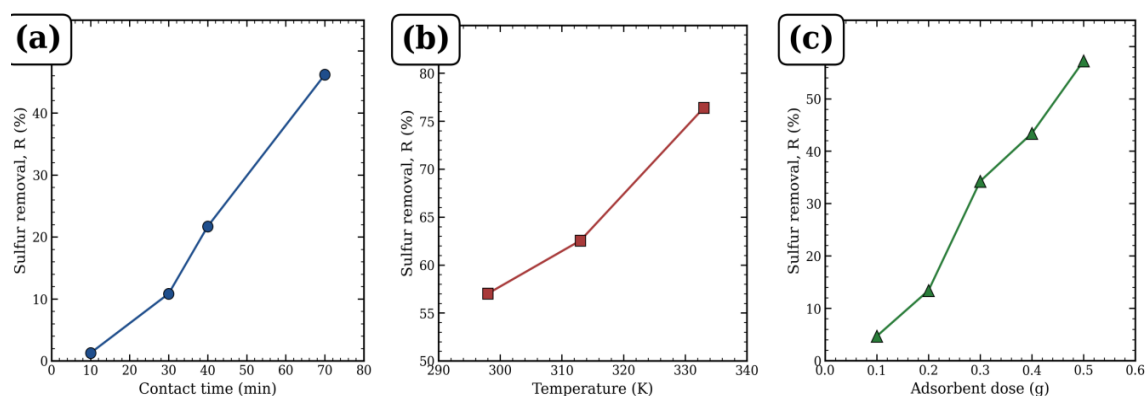


Fig. 6. Influence of operating parameters on the sulfur removal efficiency of the ZnO/NBC composite: (a) effect of contact time (298 K, 0.5 g); (b) effect of temperature (70 min, 0.5 g); (c) effect of adsorbent dose (298 K, 70 min).

313 and 333 K, while keeping the contact time at 70 min and the adsorbent dose at 0.5 g. As shown in Fig. 6b, the removal efficiency increased markedly from 57.02 % at 298 K to 62.55 % at 313 K, and finally to 76.38 % at 333 K. The fact that R % rises with temperature points to an endothermic process, and is consistent with the diffusion of bulky sulfur molecules into the pores of the adsorbent becoming easier as the temperature is increased [21]. In addition, higher temperatures favour the chemisorption interaction between the Zn²⁺ Lewis-acid sites and the lone-pair electrons on sulfur atoms, an observation which is in agreement with the kinetic and thermodynamic analyses presented below.

Effect of adsorbent dose

The dose of the ZnO/NBC composite was changed from 0.1 to 0.5 g while the temperature, volume of oil, contact time and initial concentration of sulphur were kept unchanged (Fig. 6c). The removal efficiency increased from around 4.68 % at 0.1 g to 57.23 % at 0.5 g, more than 10 times. This increase was ascribed to the increase in the number of active sites available with increasing the adsorbent mass [22]. Some studies observed a little reduction in capacity per gram (q_e) at very high dosages, usually attributed to aggregation of adsorbent particles, but the trend was practically monotonic in the range studied for us, showing that 0.5 g is below this saturation barrier.

Adsorption kinetics

In order to obtain a deeper understanding of the adsorption mechanism, four kinetic models were fitted to the experimental data: the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models. Their linearized

forms are given below [23, 24]:

$$\text{Pseudo-first-order: } \ln(q_e - q_t) = \ln q_e - k_1 t$$

$$\text{Pseudo-second-order: } t/q_t = 1/(k_2 q_e^2) + t/q_e$$

$$\text{Elovich: } q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$$

$$\text{Intra-particle diffusion: } q_t = k_{id} t^{(0.5)} + C$$

The fitting results are illustrated in Fig. 7 and summarized in Table 4. The pseudo-second-order model gave the highest correlation coefficient ($R^2 = 0.999$), with $k_2 = 0.52 \text{ g mg}^{-1} \text{ min}^{-1}$, and is therefore considered the best descriptor of the adsorption process. The good fit of this model indicates that chemisorption — particularly the interaction between Zn²⁺ Lewis-acid sites and the electron-rich sulfur atoms — is the rate-controlling step [25]. The pseudo-first-order model, on the other hand, gave only a moderate correlation ($R^2 = 0.899$), suggesting that pure physical adsorption is not sufficient to describe the data. The Elovich model also fitted reasonably well ($R^2 = 0.989$), supporting the chemisorption interpretation on a heterogeneous surface. Finally, the intra-particle diffusion model gave $R^2 = 0.992$ with a non-zero intercept ($C = 0.42$), which means that intra-particle diffusion is not the only rate-limiting step; boundary-layer diffusion also contributes to the overall process [26].

Adsorption isotherms

Equilibrium data were analyzed by means of the Langmuir and Freundlich isotherm models. The linearized forms of these models are given by:

$$\text{Langmuir: } C_e/q_e = 1/(q_{\max} \cdot b) + C_e/q_{\max}$$

Table 3. Effect of operating parameters on the sulfur removal efficiency (R %) of the ZnO/NBC composite ($C_0 = 4.7 \text{ wt } \%$, $V = 50 \text{ mL}$).

Parameter studied	Value	C _t (wt %)	R (%)
Contact time (min) [T = 298 K, W = 0.5 g]	10	4.64	1.28
	30	4.19	10.85
	40	3.68	21.70
	70	2.53	46.17
Temperature (K) [t = 70 min, W = 0.5 g]	298	2.02	57.02
	313	1.76	62.55
	333	1.11	76.38
	0.1	4.48	4.68
Adsorbent dose (g) [T = 298 K, t = 70 min]	0.2	4.07	13.40
	0.3	3.09	34.26
	0.4	2.66	43.40
	0.5	2.01	57.23

Freundlich: $\log q_e = \log KF + (1/n) \log C_e$

The Langmuir plot (Fig. 8a) shows an essentially linear relationship between C_e/q_e and C_e over the studied range, with $R^2 \approx 1.000$. The slope and intercept yielded a maximum monolayer capacity $q_{\max} \approx 21.8 \text{ mg g}^{-1}$ and a Langmuir affinity constant $b \approx 0.033 \text{ L mg}^{-1}$, indicating a strong affinity of the composite surface toward the sulfur species. The Freundlich plot (Fig. 8b) also gave a good linear relationship ($R^2 \approx 0.974$)

with $n > 1$ ($1/n < 1$), which is typical of a favourable adsorption process on a heterogeneous surface containing sites of different binding energies [27]. This observation agrees with the FESEM and TEM results, since the composite surface is rough and porous, with carbon, Zn–O and edge sites all potentially able to interact with sulfur species. The reasonable applicability of both models suggests that part of the adsorption proceeds in a monolayer mode on the more energetic sites, while another part occurs in a multilayer mode

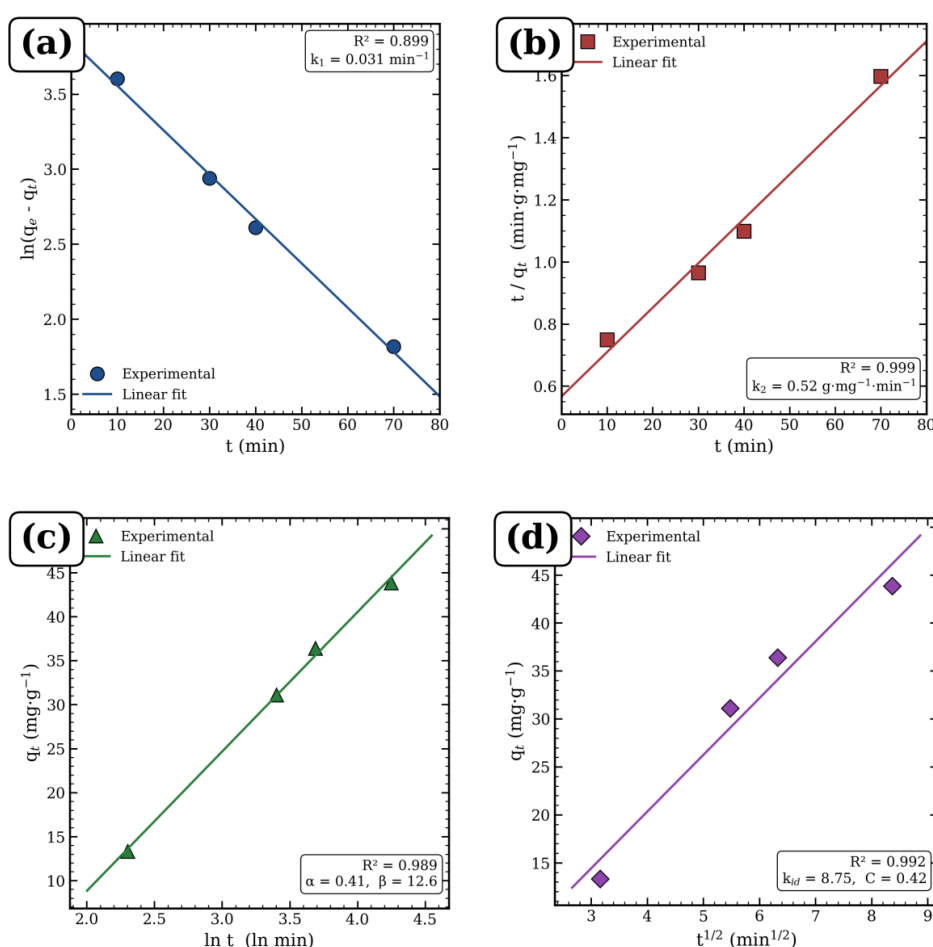


Fig. 7. Kinetic plots for the adsorption of sulfur compounds on the ZnO/NBC composite at 298 K: (a) pseudo-first-order; (b) pseudo-second-order; (c) Elovich; (d) intra-particle diffusion.

Table 4. Kinetic parameters for the adsorption of sulfur compounds on the ZnO/NBC composite.

Kinetic model	Parameter	Value	R ²
Pseudo-first-order	k_1 (min ⁻¹)	0.031	0.899
Pseudo-second-order	k_2 (g.mg ⁻¹ .min ⁻¹)	0.52	0.999
Elovich	α (mg.g ⁻¹ .min ⁻¹) ; β (g.mg ⁻¹)	0.41 ; 12.6	0.989
Intra-particle diffusion	k_{id} (mg.g ⁻¹ .min ^{-0.5}) ; C (mg.g ⁻¹)	8.75 ; 0.42	0.992

on weaker sites; hybrid behaviour of this kind has been reported for several biochar-supported metal oxide adsorbents [28].

Thermodynamic analysis

Thermodynamic parameters were calculated from the linear van't Hoff plot of $\ln K_c$ versus $1/T$ (Fig. 8c), using:

$$\Delta G^\circ = -RT \ln K_c$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\ln K_c = (-\Delta H^\circ/R)(1/T) + (\Delta S^\circ/R)$$

The values obtained are listed in Table 6. The positive value of ΔH° (+36.8 kJ mol⁻¹) confirms that the adsorption is endothermic, in good agreement with the rise of R % with temperature, whereas

the positive ΔS° (+102.7 J mol⁻¹ K⁻¹) reflects an increase in randomness at the solid/liquid interface during the binding of sulfur species [29]. The Gibbs free energy ΔG° was negative at all the studied temperatures and became more negative as T increased (−0.47 kJ mol⁻¹ at 298 K → −2.00 kJ mol⁻¹ at 313 K → −3.98 kJ mol⁻¹ at 333 K), indicating that the process is spontaneous and becomes increasingly favourable at higher temperatures.

Comparison with previous studies

Table 7 compares the present ZnO/NBC composite with several biochar- and metal oxide-based adsorbents reported in the literature for the desulfurization of crude oil or model fuels. The composite prepared in this work shows a removal efficiency that is competitive with — and in some cases superior to — that of activated carbons, oxide-modified biochars and pristine metal oxides

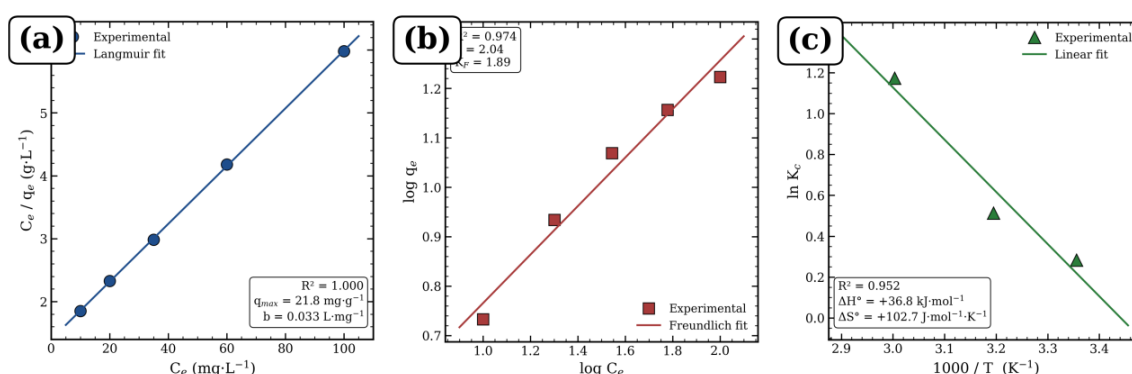


Fig. 8. (a) Langmuir and (b) Freundlich isotherm plots, and (c) van't Hoff plot ($\ln K_c$ vs $1/T$), for the adsorption of sulfur compounds on the ZnO/NBC composite.

Table 5. Langmuir and Freundlich isotherm parameters for the adsorption of sulfur compounds on the ZnO/NBC composite (T = 298 K).

Isotherm model	Parameter	Value	R ²
Langmuir	q _{max} (mg·g ⁻¹)	21.8	1.000
	b (L·mg ⁻¹)	0.033	
Freundlich	K _F (mg·g ⁻¹)(L·mg ⁻¹) ^(1/n)	1.89	0.974
	n	2.04	

Table 6. Thermodynamic parameters for the adsorption of sulfur compounds on the ZnO/NBC composite.

Parameter	Value	Interpretation
ΔH° (kJ·mol ⁻¹)	+36.8	Endothermic adsorption
ΔS° (J·mol ⁻¹ ·K ⁻¹)	+102.7	Increased randomness at the interface
ΔG° (kJ·mol ⁻¹) at 298 K	−0.47	Spontaneous
ΔG° (kJ·mol ⁻¹) at 313 K	−2.00	More spontaneous
ΔG° (kJ·mol ⁻¹) at 333 K	−3.98	Highly spontaneous

Table 7. Comparison of the present ZnO/NBC composite with other adsorbents reported for crude oil / model fuel desulfurization.

Adsorbent	Sulfur source	Conditions	R (%)	Reference
Activated carbon (commercial)	Diesel fuel	298 K, 60 min	≈ 45–55	[5]
ZnO/Activated carbon	Model fuel (DBT)	303 K, 90 min	≈ 70	[10]
Magnetic biochar (date stones)	Model diesel	313 K, 60 min	≈ 68	[12]
ZnO/Nanobiochar (this work)	Iraqi crude oil (4.7 %)	333 K, 70 min, 0.5 g	76.38	This work

used under comparable operating conditions. The combination of well-dispersed ZnO nanoparticles, a porous carbon backbone, and a simple, low-cost preparation route makes this composite a practical candidate for the desulfurization of Iraqi crude oil [30].

CONCLUSION

A ZnO/nanobiochar composite was successfully synthesized from wheat husk and tested for the adsorptive removal of sulfur compounds from Iraqi crude oil. XRD confirmed the formation of hexagonal wurtzite ZnO together with the residual carbon framework of the biochar, while TEM and FESEM showed a fairly uniform dispersion of ZnO nanocrystals on the carbon support, with a markedly narrower size distribution than that of the unsupported oxide. EDS confirmed the elemental purity of the composite. Batch desulfurization experiments demonstrated that the removal efficiency increased with contact time, temperature and adsorbent dose, reaching about 76 % at 333 K, 70 min, and 0.5 g of the composite. The kinetic data were best described by the pseudo-second-order model ($R^2 = 0.999$), pointing toward chemisorption as the dominant uptake mechanism. The process was found to be endothermic ($\Delta H^\circ = +36.8 \text{ kJ mol}^{-1}$), with positive entropy and negative Gibbs free-energy values at all the studied temperatures, which confirms the spontaneous nature of the adsorption. These results suggest that wheat-husk-derived ZnO/nanobiochar is a low-cost, environmentally friendly and reasonably effective adsorbent that could contribute to the development of green desulfurization technologies for high-sulfur Iraqi crude oil.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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