

Preparation of Nano-magnetic CuO-Fe₃O₄/Clinoptilolite as Adsorbant for Removal of Sulfur Compounds from Petrochemical and Petroleum Refinery Wastewater

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ABSTRACT

A new nanocomposite material based on copper oxide-magnetite/carbonaceous clinoptilolite (CuO-Fe₃O₄/Clinoptilolite (CP)) was prepared for the purpose of removal of sulfur from spent caustic effluents through the method of co-precipitation in the current study. The structural and morphological features of the produced sorbent were investigated using FT-IR, SEM, TEM, and BET methods, and the size of crystalline particles was estimated in the range of 48-98 nm according to XRD analysis. Optimization of the process parameters such as pH value, contact time, sorbent dose, and initial concentration of sulfur was carried out with RSM using Box-Behnken design. It was revealed that the synthesized nanocomposite CuO-Fe₃O₄/CP is characterized by high sorption properties concerning removal of sulfur compounds from refinery wastewater. At pH = 11, sorbent dose 0.3 g/L, and initial concentration 270 mg/L the efficiency of sulfur removal is 75%. According to statistical analysis there was a significant interaction among parameters, and the dose of sorbent and contact time were established as influential parameters in the sorption process. Moreover, it was found that the mechanism of sulfur adsorption on this nanocomposite is in accordance with the Langmuir and pseudo-first-order models.

KEYWORDS: Spent caustic; Sulfur compounds; Adsorption; Magnetic CuO-Fe₃O₄, Clinoptilolite; Box-Behnken design

1. Introduction

The sulfur compounds present in petrochemical waste water constitute various difficulties because they can be toxic, corrosive, and pungent [1, 2]. These caustic effluents are the result of petrochemical process that consists of various compounds of sulfur that are usually hard to remove using conventional methods [3]; therefore, there are risks involved when disposing of such compounds into the environment [4].

Even though there are various methods, including biological and chemical oxidation and adsorption, have been used for treating sulfur contamination [5, 6], adsorption is one of the most efficient methods because of its cost-effectiveness and convenience [7].

Recent research efforts have been centered around the use of magnetic adsorbents since these materials inherently have the property of being magnetically separable from the liquid phase [8].

Natural zeolites like clinoptilolite (CP) have been extensively utilized in adsorption operations owing to their chemical stability, ion-exchange properties, and high specific surface area [9]. In addition to increasing the specific surface area, the introduction of CuO nanoparticles to the CP material provides active sites which improve interactions between the adsorbent and sulfide compounds [10]. Moreover, incorporation of the magnetic Fe₃O₄ nanoparticles allows effective magnetic separation of the composite thus simplifying the regeneration procedure [11].

Nevertheless, a development of adsorbents that combine high affinity towards sulfur, stability and regenerability is still required. The current methods of adsorbent development are restricted to synthesis of magnetic zeolites that do not possess enough adsorption capabilities for sulfides or metal oxides, which tend to agglomerate and can be difficult to separate on an industrial scale [11, 12]. Therefore, it is essential to determine a method for obtaining a material that would contain all these qualities.

To address this gap, the present paper reports the synthesis of a novel ternary $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ nanocomposite aimed at the efficient removal of sulfur compounds from petrochemical or refinery wastewater. A unique feature of this research is the use of a combination of three distinct components, which overcomes the limitations associated with mono- and binary-component nanocomposites. In particular, CP acts as an environmentally friendly material and as a matrix with a large surface area that assists in the reduction of the problem of particle agglomeration found in pure $\text{CuO/Fe}_3\text{O}_4$ nanocomposites. The other advantage associated with the inclusion of Fe_3O_4 is its property of magnetism, which enables quick separation from the liquid phase and improved effectiveness of zeolite adsorbents by solving the problem of separation. In addition, CuO nanoparticles are used in order to develop active sites for the chemisorption of sulfur compounds. Unlike conventional adsorbents, this structure is designed to overcome inherent drawbacks such as low adsorption capacity and difficult separation processes.

2. Materials and methods

2.1. Materials

Wastewater from a local petrochemical plant, having undergone preliminary treatment, was collected as spent caustic. CP Natural clinoptilolite was acquired from the company called Afrand Toska. It was obtained from the natural zeolite mine in Semnan province, Iran. Zeolite was then washed using distilled water and was dried in the oven at 105°C for 12 hours. Copper oxide was prepared from copper (II) nitrate trihydrate, while iron oxide was prepared from iron (II) chloride tetrahydrate and iron (III) chloride hexahydrate.

2.2. Preparation of $\text{CuO-Fe}_3\text{O}_4/\text{CP}$

To evaluate the synergistic effects of the

components, the nanocomposites were synthesized via a sequential two-step procedure:

Step 1: Synthesis of $\text{Fe}_3\text{O}_4/\text{CP}$ (Binary Composite).

A solution of pre-treated CP in 100 mL of distilled water along with the addition of 5 g of CP was thoroughly stirred for 30 minutes. Next, 100 mL of a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.99 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.40 g) in distilled water, which was already degassed with nitrogen (N_2) gas, was added to the CP solution. 1 M of NaOH solution was gradually added at 80°C to increase the pH value to about 10. This mixture was kept at these conditions for one hour. Finally, $\text{Fe}_3\text{O}_4/\text{CP}$ was obtained by drying the product in a furnace at 450°C . Fe_3O_4 particles were also prepared in the same way, except that no CP was added [13, 14].

The precipitate was maintained under the same conditions for one hour (aging process). Finally, the product was dried in a furnace at 450°C to obtain $\text{Fe}_3\text{O}_4/\text{CP}$. Pure Fe_3O_4 particles were also prepared using a similar method, without the addition of CP [13, 14].

Step 2: Synthesis of $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ (Ternary Composite).

The prepared $\text{Fe}_3\text{O}_4/\text{CP}$ material was used as the precursor for the synthesis of the ternary nanocomposite. A copper nitrate solution ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; 1.21 g in 100 mL of distilled water) was gradually added to the $\text{Fe}_3\text{O}_4/\text{CP}$ colloidal solution under continuous stirring at pH 10 and 90°C for 2 hours, followed by magnetic separation. Finally, the resulting product was calcined in a muffle furnace at 450°C [15, 16].

2.3. Characterization of the Adsorbent

The physico-chemical properties of the prepared nanocomposites were studied. Functional groups were determined using the FT-IR spectroscopy technique, whereas surface morphology was observed through SEM. The BET approach was applied to study the surface area of the materials.

2.4. Determination of Total Organic Sulfur

The determination of total organic sulfates was conducted using an oxidation approach which converts all organic sulfates into sulfate ions. This was done by oxidizing 10 mL of the wastewater sample using 2 mL of H_2O_2 (30%) and 1 mL of HCl concentrated at 100°C for 1 hour. After cooling, the pH was adjusted and the concentration of the sulfates determined by measuring the absorption using the

methylthymol blue (MTB) reagent according to the standard ASTM E257.

On the other hand, in the colorimetric analysis, 5 mL of sample or the standard solution (containing SO_4^{2-} ions between 0 to 20 mg/L) was treated with 0.5 mL of the MTB reagent. The preparation of the reagent is done by dissolving 0.04 g of MTB and 8 g of NaCl in 10 mL of 1M HCl followed by making up the solution to 500 mL by distilled water. Furthermore, 0.5 mL of 10% BaCl_2 solution was quickly added to the solution after agitation using a vortex mixer. Absorbance was then determined at 460 nm wavelength within 10 minutes using distilled water as blank solution. Finally, the organic sulfur content (expressed as S) was calculated based on the difference between the total sulfur present after oxidation and the initial (background) sulfate concentration.

2.5. Batch Adsorption Experiments

In batch experiments, the influence of the following variables was studied:

pH (8 - 11), adsorbent dose (0.1 - 0.3 g/L), and initial concentration of pollutant (180 - 360 mg/L). For each variable, certain amounts of adsorbent were added to 50 ml of organic sulfur solution in 100 ml Erlenmeyer flasks. pH of the solution was changed by using 0.1 M HCl and NaOH. Samples were stirred for 180 min at the speed of 200 rpm at the temperature of 25°C. Upon completion of the process, the mixture underwent centrifugation and filtration. The residual

pollutant concentration was measured and analyzed using UV-Vis spectrophotometry, as described in previous sections.

The removal efficiency (R%) and adsorption capacity (q_e) were calculated using the following equations:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

Where, C_0 and C_e represent the initial and equilibrium concentrations (mg/L), respectively; V represents the solution volume (L); and m represents the adsorbent mass (g). Removal efficiency (R%) was used as the response variable for optimization via the Box-Behnken design (BBD) method. To ensure experimental reproducibility, all adsorption studies (isotherms, kinetics, and optimization) were performed in triplicate ($n=3$), and data were reported as mean $\pm$ standard deviation. Data precision was assessed using the RSD% index.

2.6. Experimental Design and Statistical Analysis

The optimization of the adsorption process and the investigation of the synergistic effects of three factors were carried out using the Box-Behnken design (BBD). This design comprised 15 experiments (runs),

Table 1. Box-Behnken design matrix with actual factor levels.

Run	PH (X_1)	adsorbent dosage (X_2)	initial concentration (X_3)	R% Experimental	R% Predict
1	9.5	0.2	270	12.10	11.9762
2	9.5	0.3	180	47.22	48.8416
3	11	0.2	360	26.90	26.6779
4	8	0.2	360	9.30	10.4454
5	8	0.2	180	19.07	16.8429
6	9.5	0.1	360	33.40	31.8141
7	9.5	0.2	270	11.90	11.9762
8	11	0.3	270	75.60	73.8634
9	8	0.1	270	45.30	47.0009
10	11	0.1	270	18.70	19.2834
11	9.5	0.1	180	15.60	14.9016
12	8	0.3	270	14.30	13.6809
13	9.5	0.3	360	18.40	19.1341
14	11	0.2	180	31.70	33.0754
15	9.5	0.2	270	12.00	11.9762

including three center points to assess experimental error. The coded and actual levels of all factors are presented in Table 1.

Analysis of variance (ANOVA), the coefficient of determination (R^2), and Pareto chart analysis were employed to identify significant model terms and evaluate the model's adequacy. The correlation between the response variable (Y) and the independent variables was established using a second-order polynomial equation (Equation 3):

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where β_0 is the intercept, β_i represents the linear coefficient of factor X_i , β_{ii} denotes the quadratic coefficient, β_{ij} signifies the interaction coefficient between factors X_i and X_j , and ε is the residual error [22].

3. Results and Discussion:

3.1. Characterization of the Adsorbent

The structural and surface properties of the synthesized magnetic $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ composite were thoroughly investigated using several complementary techniques, as detailed in the following sections.

3.1.1. Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of natural CP and the prepared composite are shown in Fig. 1. The FT-IR spectrum of the natural CP sample exhibits characteristic absorption bands associated with the zeolitic aluminosilicate framework structure. More

specifically, a wide band appearing at $3400\text{--}3500\text{ cm}^{-1}$ is due to vibrations of O-H stretching in water molecules (both crystalline water and adsorbed water), whereas the band observed in the region of $1630\text{--}1650\text{ cm}^{-1}$ is because of vibrations of H-O-H bending. A strong absorption band found at $1040\text{--}1080\text{ cm}^{-1}$ is attributed to the vibration of asymmetric stretching of Si-O-Si and Si-O-Al. Furthermore, two additional absorption bands in the $790\text{--}800\text{ cm}^{-1}$ and $450\text{--}500\text{ cm}^{-1}$ ranges correspond to symmetric stretching and bending vibrations of T-O-T bonds (where T = Si, Al) [17].

The FT-IR spectrum of the $\text{Fe}_3\text{O}_4/\text{CP}$ intermediate exhibits a distinct absorption peak at approximately 580 cm^{-1} , attributed to the Fe-O stretching vibration in magnetite. Upon the addition of CuO, new absorption bands emerge in the $480\text{--}520\text{ cm}^{-1}$ region due to Cu-O vibrations; this confirms the successful loading of copper oxide and magnetic nanoparticles onto the CP framework.

Compared to the spectrum of the intermediate material, the FT-IR spectra reveal significant changes during the formation of the $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ composite. A decrease in the intensity of the O-H stretching peak indicates chemical interactions between the metal oxides and the surface hydroxyl groups of the zeolite. Furthermore, minor shifts observed in the Si-O-Si stretching peaks can be attributed to strong interactions between the metal oxide phases and the aluminosilicate framework. The increased intensity in the $470\text{--}600\text{ cm}^{-1}$ region—resulting from the overlap of Fe-O and Cu-O vibrations—confirms that CuO and Fe_3O_4 have been

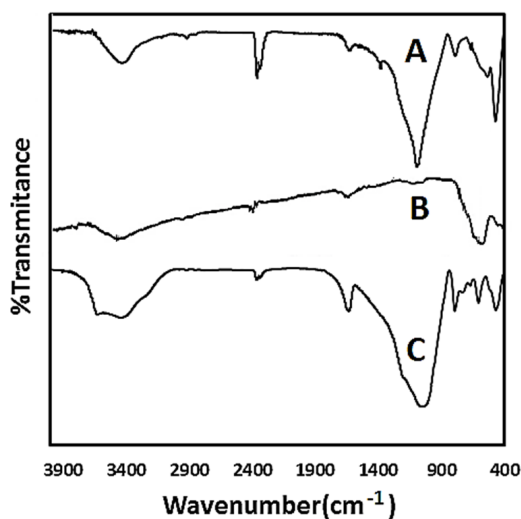


Fig. 1. The Infrared spectrum of CP(A), $\text{Fe}_3\text{O}_4/\text{CP}$ (B) and the $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ (C)

successfully anchored to the CP framework without disrupting the zeolite's parent structure [18, 19].

3. 1. 2. Morphological and Elemental Analysis (FESEM/EDX)

The surface morphology of the prepared CuO-Fe₃O₄/CP composite was examined using Field-Emission Scanning Electron Microscopy (FESEM), as shown in Fig. 2. As observed in the FESEM images, the surface exhibits a highly porous and rough topography—a characteristic highly desirable for adsorption applications due to the increased number of active sites. The CuO and Fe₃O₄ nanoparticles, with an average size of approximately 50 nm, appear to be well-dispersed and uniformly distributed within the CP structure. No signs of agglomeration (particle clustering) or structural cracks are evident, indicating effective process control.

Furthermore, the chemical composition of the composite was analyzed using Energy-Dispersive X-ray (EDX) spectroscopy. The EDX results reveal the presence of Fe, Si, Cu, Al, and O as major

elements, along with a small amount of C as a minor element, confirming the successful attachment of the nanoparticles onto the aluminosilicate substrate. Overall, the morphological findings from the FESEM and EDX analyses demonstrate good consistency and agreement between the results.

3. 1. 3. Transmission Electron Microscopy (TEM)

The morphology and distribution of CuO-Fe₃O₄ nanoparticles immobilized on the CP framework were investigated using transmission electron microscopy (TEM) (Fig. 3). The TEM image reveals that the CuO and Fe₃O₄ nanoparticles have been successfully incorporated into the zeolitic matrix, appearing as small, irregular clusters with a distinct size distribution at the nanoscale. The distinct contrast in electron density between the zeolitic framework (lower density) and the metal oxide nanoparticles (darker, higher electron density) confirms the successful immobilization of the metal phases on the CP surface. This high degree of dispersion—evidenced by the absence of large agglomerates—is

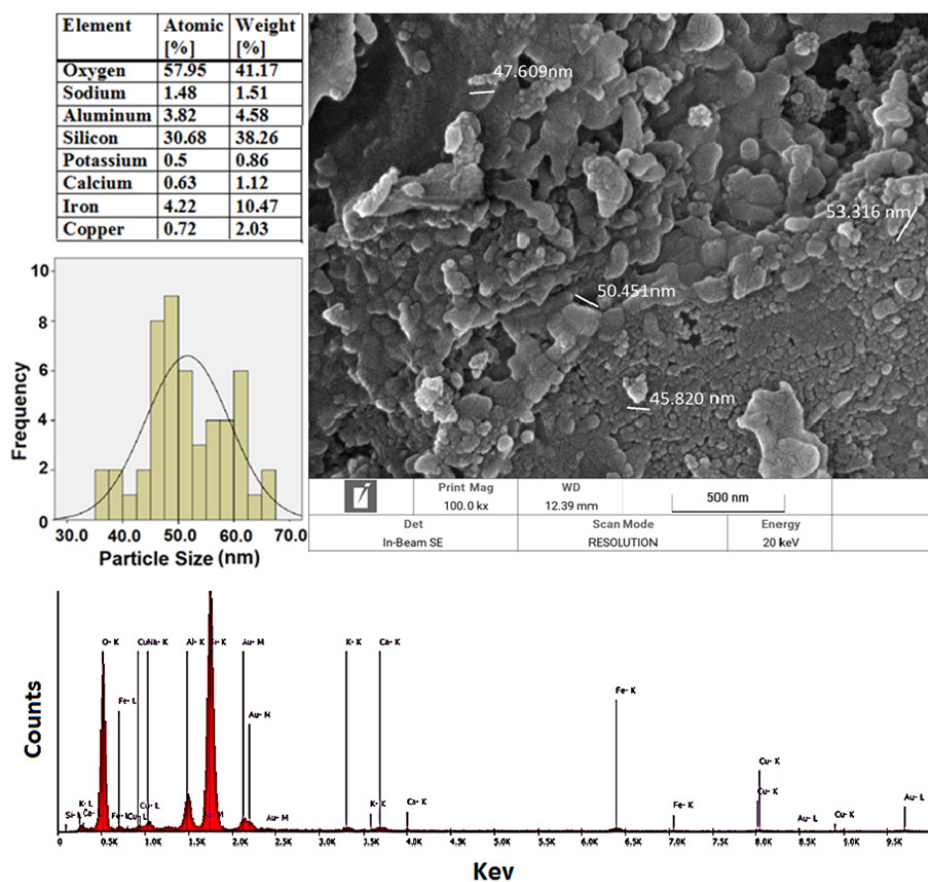


Fig. 2. FESEM/EDX and elemental analysis of CuO-Fe₃O₄/CP

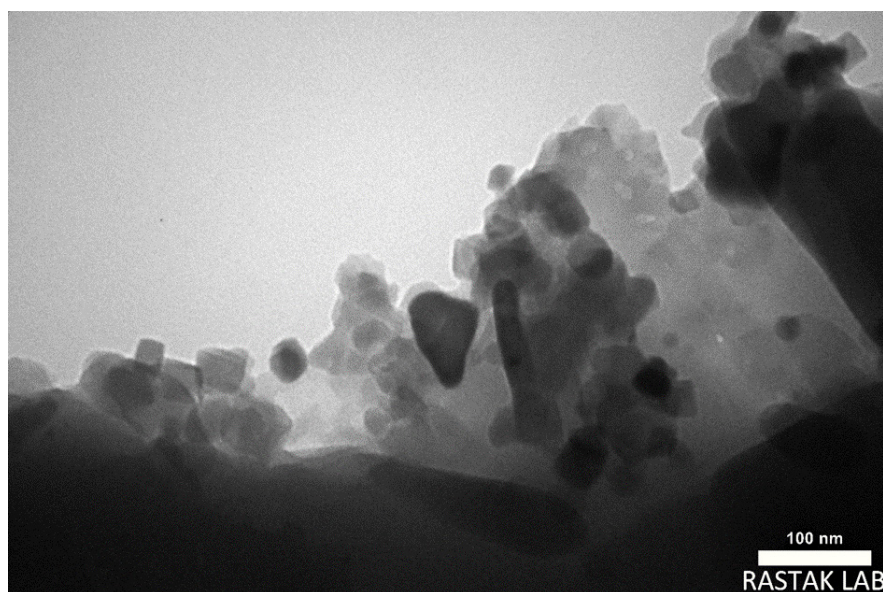


Fig. 3. TEM image of CuO-Fe₃O₄ immobilized on CP

Table 2. The information related to the synthetic sample obtained by nitrogen adsorption and desorption method

Sample	BET surface area(m ² /g)	Average pore diameters (nm)	Total pore volume(cm ³ g ⁻¹)
Cp	28.384	15.796	0.1121
Fe ₃ O ₄ /Cp	18.567	9.594	0.0603
CuO-Fe ₃ O ₄ /Cp	14.5	7.0436	0.0255

crucial for maximizing accessibility to active sites and, consequently, enhancing the material's overall performance in the adsorption process.

3.1.4. Textural Properties (BET Analysis)

The textural properties of the pure CP sample and the CuO-Fe₃O₄/CP nanocomposites were investigated using nitrogen (N₂) adsorption-desorption isotherms (see Fig. 4). These isotherms exhibit Type IV behavior (according to IUPAC classification), characterized by a significant hysteresis loop resulting from capillary condensation in mesoporous materials. Initial nitrogen uptake at low relative pressures ($P/P_0 < 0.3$) indicates the presence of micropores—an intrinsic feature of CP—while the sharp increase in nitrogen uptake at high relative pressures signifies the formation of mesopores. The formation of this pore system—comprising a combination of original micropores and newly formed mesopores—results from the successful deposition of CuO and Fe₃O₄ nanoparticles onto the zeolite surface [20].

Pore size distribution analysis reveals a dominant mesopore diameter, indicating that the modification has created a hierarchical porous structure that facilitates mass transfer and enhances accessibility to active adsorption sites. Data regarding textural properties—including BET specific surface area, total pore volume, and average pore diameter—are presented in Table 2.

In this regard, the results indicated a reduction in surface area and pore volume following the modification process. As previously noted, the surface area decreased from 28.38 m²/g for the CP sample to 18.57 m²/g for the Fe₃O₄/CP sample, and further to 14.50 m²/g for the CuO-Fe₃O₄/CP composite. Additionally, the pore diameter was reduced from 15.80 nm to 7.04 nm. This reduction in properties can be primarily attributed to the partial blockage of zeolite channels and the presence of Fe₃O₄ and CuO nanoparticles within the pore structure. It is worth noting that the preservation of mesoporous structural

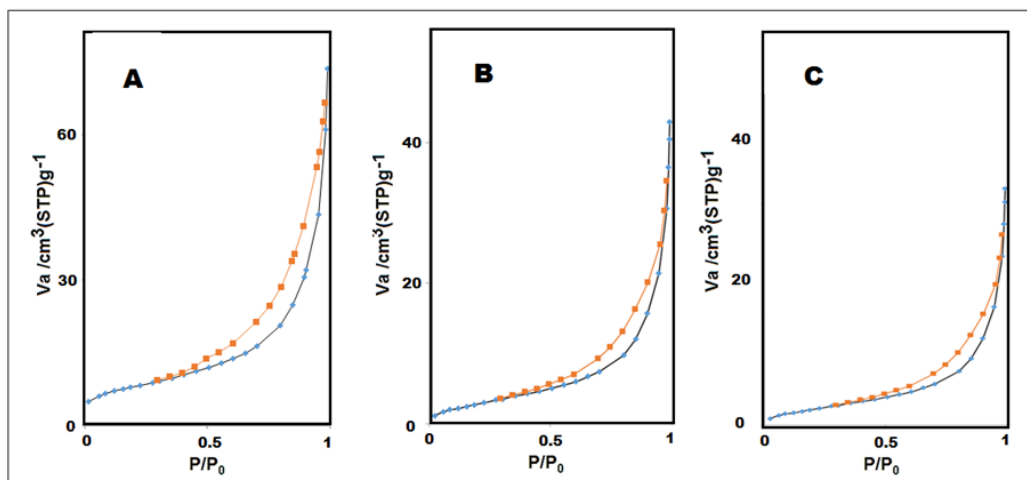


Fig. 4. Nitrogen gas adsorption and desorption curve for CP (A), $\text{Fe}_3\text{O}_4/\text{CP}$ (B) and $\text{CuO-Fe}_3\text{O}_4/\text{CP}$

characteristics—despite the aforementioned reductions—demonstrates the successful loading of $\text{CuO-Fe}_3\text{O}_4$ nanoparticles onto the CP framework.

3.1.5. X-ray Diffraction (XRD) Analysis

The crystallinity and phase composition of the $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ sample were investigated using X-ray diffraction (XRD); the results are presented in Fig. 5. The XRD results indicate the presence of crystalline phases characteristic of CP, Fe_3O_4 (spinel), and CuO (monoclinic). The diffraction peaks show excellent agreement with standard JCPDS references for Fe_3O_4 (JCPDS card no. 96-900-7645) and CuO (JCPDS card no. 00-041-0254). The retention of the CP diffraction peaks demonstrates that the incorporation of the metal and magnetic oxides caused no significant structural damage to the zeolite framework.

To determine the average crystallite size (D), the Scherrer equation was used:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

Here, K is the dimensionless shape factor (0.9), λ is the X-ray wavelength (0.15405 nm for $\text{CuK}\alpha$ radiation), β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ is the Bragg angle.

Crystallite size was estimated using various methods. Calculations based solely on the most intense diffraction peak indicated an average CuO crystallite size of approximately 98 nm; however, considering the FWHM of all diffraction peaks

yielded an average crystallite size of 48 nm. This discrepancy indicates a degree of heterogeneity in the crystallite size distribution within the composite material. Furthermore, the value obtained using the FWHM of all diffraction peaks is more accurate and closer to the particle size determined via SEM.

Based on Scanning Electron Microscopy (SEM) results, the average particle size of the synthesized $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ composite is approximately 50 nm (Fig. 2). Conversely, X-ray diffraction (XRD) analysis indicated an average crystallite size of 48 nm. Observing crystallite sizes in XRD that are similar to—or even larger than—the particle sizes measured by SEM stems from the inherent differences between the two techniques: SEM determines the actual particle size, whereas XRD measures the crystallite size. This discrepancy may arise from any of the following factors: (1) the presence of larger crystallites within the particles observed via SEM, (2) the influence of lattice strain on XRD peak broadening, or (3) the presence of distinct crystalline phases. Despite these differences, the crystallite size results indicate a high degree of nanostructural order, which contributes to a favorable specific surface area.

3.2. Adsorption Mechanism

To analyze the synergy exhibited by the composite material, the functions performed by each of its components must be understood. The CP material acts as a porous matrix with a high surface area, possessing a high density of ion-exchange sites and aluminosilicates for the initial trapping of

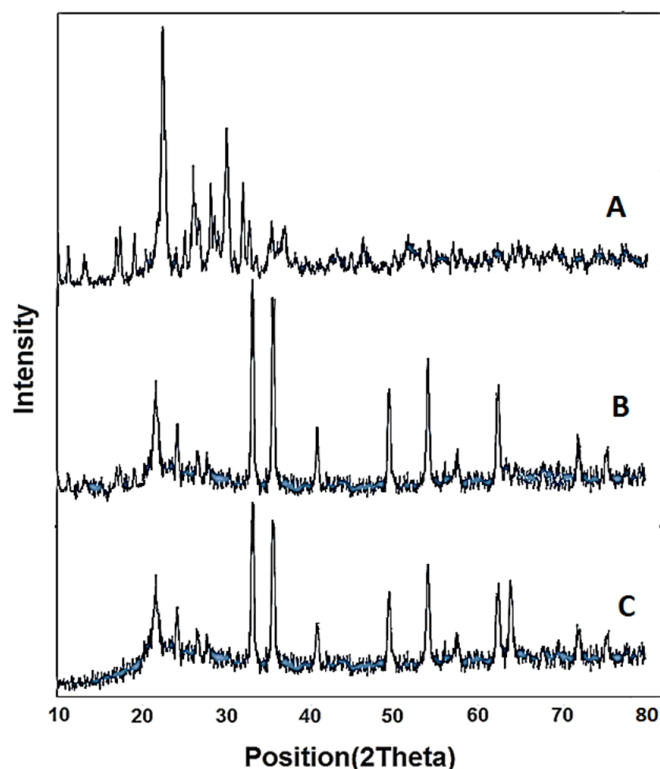


Fig. 5. XRD patterns of CP(A), $\text{Fe}_3\text{O}_4/\text{CP}$ (B) and $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ (C)

pollutants [12, 17]. Fe_3O_4 nanoparticles impart superparamagnetic properties to the composite, enabling easy magnetic separation from treated wastewater—a crucial requirement for industrial-scale applications. Furthermore, CuO nanoparticles serve as active sites for enhanced adsorption; chemisorption occurs due to the presence of Cu^{2+} ions and oxygen vacancies within the CuO.

3. 3. Optimization of Adsorption Process via Response Surface Methodology (RSM)

The Box-Behnken design (BBD) method was employed to determine the individual and combined effects of factors on removal efficiency (R%). Three factors—pH, adsorbent dosage, and initial pollutant concentration—were rigorously investigated (Table 1) [21]. Response Surface Methodology (RSM) was utilized as an effective approach to analyze the complex, non-linear interactions among the variables [21, 25].

Experimental results demonstrated that adsorption behavior is significantly dependent on operational parameters. Among the parameters studied, pH was found to have a substantial impact on removal

efficiency. As the pH increased from 9.5 to 11—while keeping the dosage and concentration constant (at 0.2 g and 270 mg/L, respectively)—high removal efficiency was observed, resulting in an increase in R% from approximately 12% to 26.90%. This rise in efficiency accompanying the increase in pH may be attributed to a more negatively charged adsorbent surface and reduced competition between protons and the adsorbate molecules.

Increasing the adsorbent dosage from 0.1 to 0.3 g resulted in a positive trend regarding the removal percentage (R%), as the availability of a greater number of active sites facilitates the process. However, the absence of a strictly linear relationship suggests the potential negative impact of factors such as site saturation or adsorbent particle agglomeration at dosages exceeding the optimum level. Another factor inversely related to removal efficiency was the initial concentration. Although moderate concentrations in the 180–270 mg/L range yielded favorable results, higher initial concentrations (e.g., 360 mg/L) led to a significant drop in removal percentage to 9.30% (at pH 8 and an adsorbent dosage of 0.2 g). This phenomenon can be attributed to the saturation

of active sites resulting from an increased ratio of adsorbate to adsorbent sites.

In addition to the aforementioned dependencies, the interactive effects of pH and concentration, as well as adsorbent dosage and concentration, were identified. In this regard, the BBD method enabled the determination of the process's optimal operating range. The highest removal efficiency (75.60%) was observed at pH 11, an adsorbent dosage of 0.3 g, and an initial concentration of 270 mg/L.

3.4. Statistical Analysis of the RSM Model

The statistical significance of the model was determined using Analysis of Variance (ANOVA), as shown in Table 3. The model yielded a very high F-value of 219.64 ($p < 0.0001$), indicating statistical significance and confirming that the observed differences were not due to random error. A coefficient of determination (R^2) of 99.55% and an adjusted R^2 of 99.9% were obtained, demonstrating a favorable correlation between the experimental results and the developed model.

It is worth noting that, based on the analysis of variance (ANOVA), interaction effects predominated over linear effects. Specifically, the two-way interaction between pH level and adsorbent dosage ($X_1 \times X_2$) yielded the highest F-statistic (642.69), indicating that the interaction between these two variables is the most influential factor in the adsorption process. Furthermore, the significant impact of quadratic

effects points to the highly non-linear nature of the process. Although a slight “lack-of-fit” was observed, the very high coefficient of determination (R^2) and the statistical significance (p-value) of all effects confirm the model's accuracy.

3.5. Mathematical Modeling and Statistical Validation

To quantify the influence of the operating parameters, a second-order quadratic response surface model was developed. The experimental data were fitted to the following polynomial equation (Equation 5):

$$R\% = 627.2 - 106.51 X_1 - 1656.8 X_2 + 0.2235 X_3 + 4.349 X_{12} + 1669.7 X_{22} + 146.50 X_1 \times X_2 - 1.2950 X_2 \times X_3 \quad (5)$$

It was determined that pH (X_1) and adsorbent dosage (X_2) had a positive and significant effect on removal efficiency, whereas initial concentration (X_3) exerted a negative effect. This indicates that increasing alkalinity and the number of active sites enhances the process's adsorption capacity, while a high pollution load leads to their saturation.

Furthermore, interaction effects between the factors were identified. Notably, a positive and significant interaction was observed between pH and adsorbent dosage ($X_1 X_2$), implying that the effect of increasing the adsorbent dosage is much

Table 3. ANOVA for Quadratic Model Source

Source	DF	Adj ss	Adj ms	F-value	p-value
Model	7	4620.85	660.12	219.64	0.0000
Linear	3	834.84	278.28	92.59	0.0000
pH(X_1)	1	526.99	526.99	75.19	0.0000
adsorbent dosage(X_2)	1	225.99	225.99	75.19	0.0000
Initial concentration(X_3)	1	81.86	81.86	27.24	0.001
Square	2	1311.05	655.53	218.11	0.000
X_1^2	1	355.57	355.57	118.31	0.000
X_2^2	1	1035.47	1035.47	344.53	0.000
2-way Interaction	2	2474.96	1237.48	411.74	0.000
$X_1 \times X_2$	1	1931.60	1931.60	642.69	0.000
$X_2 \times X_3$	1	543.36	543.36	180.79	0.000
Error	7	21.04	3.01		
Lake-of-Fit	5	21.02	4.20	420.37	0.002
Pure Error	2	0.02	0.01		
Total	14	4641.89			
$R^2=99.55$	$R^2(\text{adj})=99.9$	$R^2(\text{pred})=96.52$			

stronger in an alkaline environment [22]. Conversely, the negative interaction between adsorbent dosage and concentration (X_2X_3) indicates that the impact of increasing the adsorbent dosage is somewhat diminished by the initial concentration [23]. The significance of the quadratic terms (X_1^2 and X_2^2) also suggests that the response surface is non-linear and exhibits curvature [24].

The adequacy of the statistical model was extensively evaluated and confirmed via ANOVA (Table 3). A high F-statistic (219.64) and a p-value of less than 0.0001 were obtained, indicating the model's high predictive power. The model's excellent performance is evidenced by the high R^2 (99.55%) and R_{adj} (99.9%) values. Model adequacy was further verified through residual analysis; the plot of predicted versus observed values demonstrated good alignment along the 45-degree line, and the normal probability plot of residuals confirmed the assumption of error normality. Overall, the quadratic model was deemed suitable and efficient for optimizing the removal of sulfur compounds via adsorption using the prepared $\text{CuO-Fe}_3\text{O}_4/\text{CP}$ adsorbent.

3.6. Surface Response Analysis and Interactive Effects

The effect of the interaction between independent variables is illustrated via 3D plots (Fig. 6). Fig. 6a

reveals that pH (X_1) is the primary, determining factor in the performance of the adsorption process. It is observed that increasing the pH from 8 to 11 leads to a significant rise in removal efficiency (R%), with the maximum efficiency (approximately 68%) achieved at a pH of 11 and an adsorbent dosage of 0.30 g. The presence of a steep slope and curvature in this region is clearly evident, indicating a positive interaction ($X_1 \times X_2$); furthermore, it can be inferred that the structural deprotonation of the adsorbent surface—which facilitates electrostatic attraction—is most efficient when the density of active sites is at its peak.

Fig. 6b illustrates the synergistic interaction between the adsorbent dosage (X_2) and the pollutant concentration (X_3). At lower adsorbent dosages, the removal percentage (R%) remains low and sensitive to variations in X_3 ; however, as the dosage reaches 0.3 g, the response surface flattens—reflecting the adsorbent's “buffering capacity,” whereby more active sites become available as the pollutant load increases. This non-linear behavior confirms the statistical significance of the interaction term ($X_2 \times X_3$) in our model. Furthermore, a distinct curvature is observed in the relationship between concentration and removal efficiency: efficiency rises with increasing concentration but subsequently levels off—a phenomenon likely attributable to the saturation of surface sites. Thus, these response surfaces demonstrate

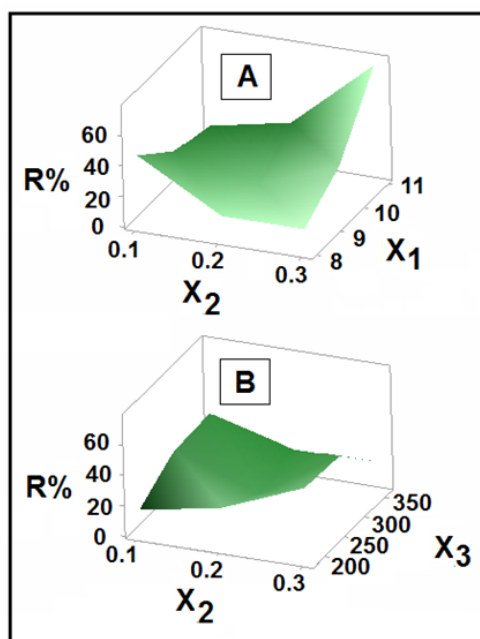


Fig. 6. Three-dimensional response surface plots showing the effect of process parameters on sulfur removal efficiency (R%): (A) Interaction between pH (X_1) and adsorbent dosage (X_2), and (B) Interaction between adsorbent dosage (X_2) and initial pollutant concentration (X_3).

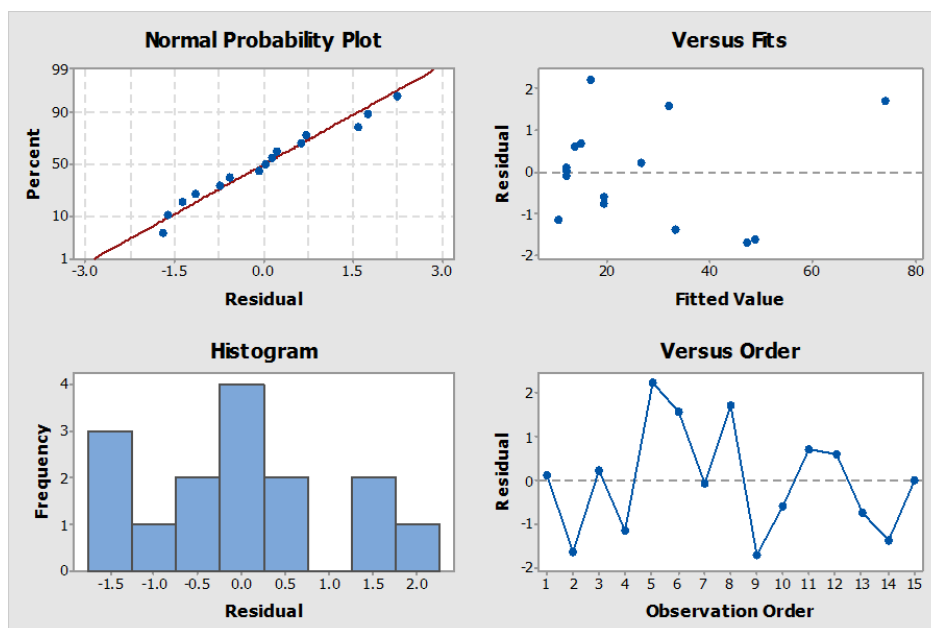
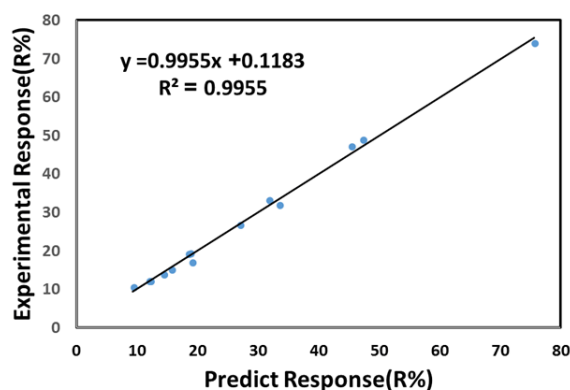


Fig. 7. Residual plots for R%

Fig. 8. Scatter plot of predicted response versus actual response for the sulfur compound- CuO-Fe₃O₄/CP adsorption system.

that the quadratic model we developed accurately predicts removal efficiency while accounting for its physical limitations.

3.7. Residual Diagnostic Analysis

To assess the statistical validity and predictive power of the developed adsorption model (concerning the adsorption of organic sulfur compounds onto the CuO-Fe₃O₄/CP adsorbent), a residual analysis was conducted. As shown in Fig. 7, the residuals exhibit a normal distribution; the normal probability plot reveals that the residual points lie along the line. Further confirmation of the normality assumption is provided by the residual histogram, which displays a

bell-shaped, relatively symmetrical profile centered at zero.

Furthermore, the plot of residuals versus fitted values demonstrates a random dispersion of residuals—indicating the absence of any systematic trend—thereby validating the assumption of constant variance and confirming that the model captures the full variation in the response (R%). Finally, the plot of residuals against observation number shows no discernible trend over time.

3.8. Model Prediction and Experimental Validation

Overall, the results above demonstrate the high reliability and efficiency of the ANOVA analysis

and the empirical model. To evaluate the predictive capability of the RSM model, a plot of predicted versus actual values was generated (Fig. 8). The proximity of data points to the $y=x$ straight line indicates a strong relationship between the two datasets. Furthermore, the model's accuracy is confirmed by the residual plot, as the majority of the residuals fall within the $\pm 10\%$ range. The good fit of the experimental data to the quadratic model demonstrates that the response surface equations can be used to predict the adsorption performance of the CuO-Fe₃O₄/CP adsorbent.

3.9. Adsorption isotherms

Adsorption isotherms are considered key parameters for studying adsorption phenomena in the fields of surface chemistry and environmental engineering. These isotherms provide information regarding adsorption capacity and the mechanism of the process. Numerous models have been introduced to describe adsorption behavior, but the Langmuir, Freundlich, and Temkin isotherms are among the most common [26-31].

3.9.1. Langmuir Isotherm

Based on the Langmuir isotherm, adsorption occurs in a monolayer on a surface with a limited number of identical sites. According to this isotherm, the adsorption process involves the placement of molecules onto homogeneous, specific sites, with no interaction occurring between the adsorbed molecules [27]. The non-linear form of the Langmuir isotherm can be represented by Equation 6.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

Where:

q_e = equilibrium adsorption capacity (mg/g), C_e = equilibrium concentration of the adsorbate (mg/L), $q_{\max}$ = adsorption capacity (mg/g), K_L = Langmuir constant related to adsorption energy (L/mg). The linearized equations of the Langmuir isotherm are as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (7)$$

This linear forms allow easy determination of and from the slope and intercept of the plotted data.

3.9.2. Freundlich Isotherm

The Freundlich isotherm is an empirical equation for the adsorption process on heterogeneous surfaces with a non-uniform distribution of adsorption heat

[28]. The non-linear form of the Freundlich isotherm is expressed in Equation 8

$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

Where:

K_F = Freundlich constant, (indicative of adsorption capacity). Linearized form (equation 9):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

Plotting versus gives a straight line with slope and intercept.

3.9.3. Temkin Isotherm

The Temkin isotherm considers the effects of indirect adsorbate-adsorbate interactions on adsorption isotherms. It assumes that the heat of adsorption decreases linearly with coverage [29]. The nonlinear form is given in equation 10.:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (10)$$

R = universal gas constant (8.314 J/mol·K) T = absolute temperature (K) K_T = Temkin constant related to heat of adsorption (J/mol) B = Temkin isotherm constant (L/g). If we take the natural logarithm of equation 10, we will arrive at the linear equation of this model in equation 11.

$$q_e = B \ln C_e + B \ln K_T \quad (11)$$

In this case, the B value is determined from equation 12.

$$B = \frac{RT}{b} \quad (12)$$

Where:

Plotting the data yields a linear curve. Conclusion: Each adsorption isotherm equation provides distinct information regarding the adsorption process, while their linearized forms facilitate parameter determination via linear regression. The appropriate equation is selected based on the specific adsorbent-adsorbate system.

To optimize the design of the adsorption system for the adsorbent in question, the Langmuir, Freundlich, and Temkin equations were employed; the corresponding plots are presented in Figs. 8(a),

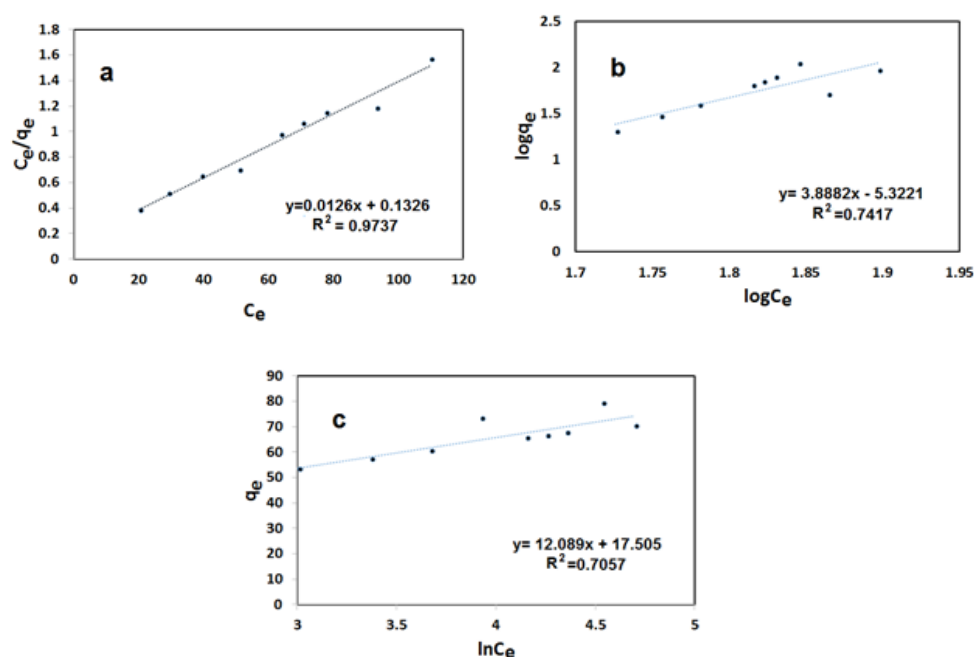


Fig. 9. Langmuir(a), Freundlich (b) and Temkin (c) isotherm models

Table 4. Langmuir, Freundlich, and Temkin isotherm model parameters and coefficients of determination for the adsorption of sulfur compounds on CuO-Fe₃O₄/CP.

Model	Parameters		Coefficient of determination
Langmuir	$K_L = 0.094$	$q_{\max} = 7.54$	$R^2 = 0.9737$
Freundlich	$K_F = 4.8 \times 10^{-5}$	$n = 0.26$	$R^2 = 0.7417$
Temkin	$K_T = 4.255$	$b = 205.047$	$R^2 = 0.7057$

8(b), and 8(c).

The maximum adsorption capacity ($q_{\max}$), calculated using the Langmuir equation, was found to be 7.54 mg/g. Another parameter indicating a high affinity between the sulfur compounds and the CuO-Fe₃O₄/CP solid surface is the Langmuir constant ($K_L = 0.094$ L/mg). Conversely, the Freundlich and Temkin models yield lower values, suggesting a uniform energy distribution across the adsorbent surface [28–31].

3. 10. Quality Control and Method Validation

To ensure the reliability and accuracy of the analytical results, rigorous quality control procedures were employed. The precision of the experimental data was evaluated using the relative standard deviation (RSD%) metric for both the equilibrium adsorption capacity (qe) and the kinetic rate constants. The results demonstrated that RSD% values did not

exceed 3.4% in any of the experiments, indicating high reproducibility and precision.

Furthermore, the accuracy of the analytical method was assessed through “spike-recovery” experiments. In these tests, known quantities of sulfur compounds were added to petroleum wastewater samples, and their recovery percentages were determined. The recovery rates for the sulfur compounds ranged from 95.4% to 102.7%. Such a high and consistent recovery range demonstrates the reliability and high reproducibility of the measurement method within the complex matrix of petroleum wastewater.

3. 11. Adsorption Kinetics

Kinetic experiments play a significant role in determining the rate-limiting step as well as the mechanism of the adsorption process [26–31]. In this study, adsorption kinetics were analyzed using PFO and PSO models.

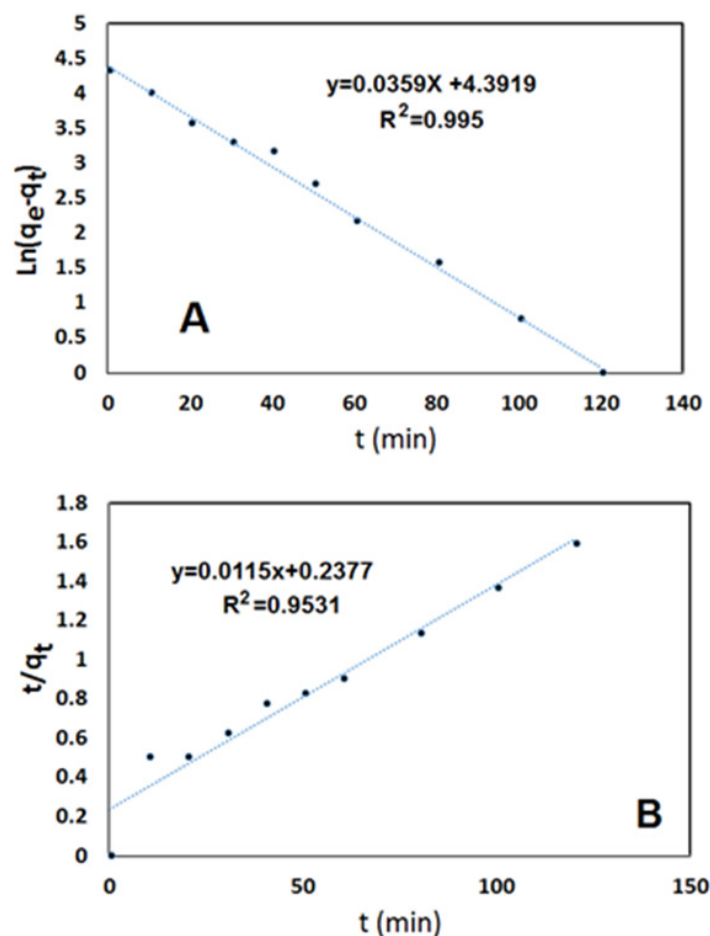


Fig. 10. Kinetic Models, Pseudo-first-order(A) Pseudo-second-order(B) kinetic model

The Pseudo First Order (PFO) model, which assumes that the adsorption rate depends directly on the number of vacant adsorption sites, is formulated as follows by Equation (13):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

The pseudo-second-order (PSO) model, which assumes that the rate-limiting step involves chemisorption—driven by valence forces through electron sharing or exchange—is expressed by Equation (14):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (14)$$

It can be seen from Fig. 10 that the adsorption process exhibits a strong correlation with the pseudo-first-order kinetic model. This indicates that the rate-limiting step of the reaction is primarily governed by

a physisorption mechanism or mass transfer, such that the adsorption rate is limited by the number of available sites on the adsorbent surface.

This enhanced adsorption capacity is attributed to the synergistic effect between the CuO and Fe₃O₄ components of the composite material. While Fe₃O₄ nanoparticles provide a recoverable magnetic adsorbent that allows for easy separation from complex petrochemical media, they also ensure the structural stability of the composite. Conversely, CuO nanoparticles serve as active sites for sulfur adsorption. This synergistic effect stems from the ability of CuO to facilitate strong chemisorption through the formation of specific Cu-S bonds. This chemical activity, combined with the rapid magnetic separation afforded by the Fe₃O₄ nanoparticles, accounts for the composite's superior adsorption efficiency compared to its individual components.

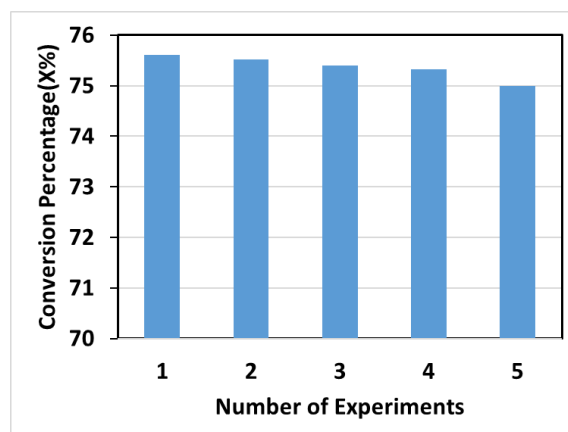


Fig. 11. Cycling performance of the CuO-Fe₃O₄/CP adsorbent for sulfur removal.

3. 12. Reusability, Stability, and Practical Implementation

However, the operational viability of any adsorbent depends on its stability and reusability. In this regard, the CuO-Fe₃O₄/CP composite demonstrated highly favorable recyclability over five consecutive adsorption-desorption cycles.

3. 12.1. Reusability and Stability:

At the end of each cycle, following the adsorption stage, the magnetic adsorbent was successfully separated using an external magnetic field. Subsequently, the desorption of the adsorbed sulfur compounds was carried out using a 0.1 M NaOH solution. After washing with distilled water and drying, the adsorbent was ready for reuse in the next cycle. As shown in Fig. 11, the composite demonstrated high efficiency in removing sulfur compounds, retaining approximately 96% of its initial capacity after five cycles. This capacity retention indicates the high structural stability of the CuO-Fe₃O₄/CP composite. The slight decrease in efficiency can be attributed to some loss of adsorbent mass during the regeneration process.

3. 13. Industrial Perspective and Scalability:

From the perspective of industrial processes, the following advantages of the proposed CuO-Fe₃O₄/CP adsorbent for the treatment of refinery wastewater may be highlighted:

1. Cost Efficiency: Due to the usage of natural CP, which is a cheap and plentiful material, the production costs of the adsorbent become noticeably lower than the costs for the production of completely artificial nanomaterials. In addition, due to the heterogeneous

structure, the catalyst ensures maximum efficiency even when there is a minimum of metal content.

2. Scalability: The magnetic properties of the adsorbent allow its fast separation from the wastewater using external magnetic fields. Thus, the usage of expensive and time-consuming high pressure filters becomes unnecessary.

3. Easy Implementation: The proposed adsorbent can be easily added to existing systems of wastewater treatment by using either fixed bed or stirred tanks reactors.

4. Regenerability and Long Lifespan: As the material was shown to be stable through multiple adsorption-desorption cycles (5 cycles), it demonstrates its regenerability. In this way, not only are the ecological problems associated with the sludge disposal solved but also the OPEX of the refinery becomes lower.

3. 14. Comparative Analysis and Performance Evaluation

To evaluate the performance of the CuO-Fe₃O₄/CP composite in comparison with other adsorbents used for the removal of organic sulfur compounds from wastewater, a comparison has been conducted and is presented in Table 5..

3. 14. 1. Performance Benchmarking

It is worth noting that the developed adsorbent not only exhibits high performance but also features a simple preparation method and desirable physical properties—factors that render it one of the most competitive adsorbents in this field. Furthermore, the maximum removal efficiency for sulfur-containing compounds reached approximately 75%, clearly demonstrating the high efficacy of the CuO-Fe₃O₄/

Table 5. Comparison of various adsorbents for the removal of sulfur compounds from wastewater.

Adsorbent Type	Target Sulfur Compounds	Matrix / Wastewater Type	Adsorption Capacity (mg/g) / Removal Efficiency (%)	Key Findings / Mechanisms	Reference
Modified Activated Carbon (MAC) (Chemically modified with HNO_3 , H_2O_2 , and thermal treatment)	Sulfur compounds (Sulfides)	Real Petroleum Refinery Wastewater	52 mg/g (2.5 times higher than unmodified carbon)	- Isotherm: Freundlich model best fit. - Kinetics: Pseudo-second-order model. - Mechanism: Intraparticle and film diffusion	[32]
Activated Carbon from Cotton Spinning Waste (Chemically activated with HNO_3 , H_2O_2 , KOH)	Sulfur compounds	Real Refinery Wastewater (Tunisian Company)	168.4 mg/g	Isotherm: Langmuir model ($R^2 = 0.98$), indicating homogeneous monolayer adsorption. - Kinetics: Pseudo-second-order, suggesting chemisorption, fractionation and adsorption. - Mechanisms: Electrostatic attraction and hydrogen bonding. - Advantage: Dual removal pathways (interfacial adsorption and foam transfer).	[33]
Amphiphilic Graphene Oxide (GO-DDA) (Functionalized with N-dodecylamine) adsorption and foam transfer).	Sulfur-containing ions ($\text{S}_2\text{O}_8^{2-}$ and SO_4^{2-})	Degraded Wastewater (Post- persulfate oxidation)	Removal Efficiency: ($\text{S}_2\text{O}_8^{2-}$) and 95.5% (SO_4^{2-}) 6.1%		[34]
Ac-ZnO/ Al_2O_3 Composite(Activated carbon with metal oxide)	Sulfur compounds(tested on Dibenzothiophene DBT)	Tested on model solutions and crude oil; not specifically in refinery wastewater	58.7 mg/g(for DBT) 66.8% improvement over pristine AC)	Function Designed removal of sulfur and other pollutants (Pb^{2+} , phenol. Isotherm: Langmuir model -Kinetics pseudo- second order. -Limitation: Not tested on real refinery wastewater	[35]

CP composite.

Regarding the analysis, it is important to highlight the discrepancy between these findings and recent studies that reported lower efficiencies. For instance, in Reference 35, the authors reported a removal rate of 58.7% under similar operating conditions. This high performance can be attributed to the synergistic effect between the high specific surface area of CP and the enhanced chemical affinity resulting from the presence of CuO nanoparticles. Unlike previous studies that focused on single-component adsorbents, we have developed a multifunctional composite.

4. Practical Implications and Scalability

The potential for industrial-scale production of the CuO-Fe₃O₄/CP composite is significantly enhanced by the availability of low-cost natural CP and the simplicity of the co-precipitation synthesis method. A major obstacle in treating large volumes of refinery wastewater is the cost-effective recovery of adsorbents. The superparamagnetic properties of the synthesized composite offer a robust solution to this challenge, enabling rapid and efficient recovery via magnetic field-assisted separation. This approach bypasses the energy-intensive filtration or centrifugation processes typically required for non-magnetic adsorbents. Furthermore, the demonstrated regeneration efficiency (96% after five cycles) points to significantly reduced operating costs (OPEX) and the potential for long-term, sustainable application. To further validate performance under actual refinery conditions, pilot-scale studies utilizing column-mode adsorption in continuous-flow systems are strongly recommended.

5. Conclusion

The present study has successfully synthesized a novel magnetic ternary system—CuO-Fe₃O₄/CP—for the efficient removal of sulfur compounds from aqueous media. The formation of this ternary system, along with the composite's porous nature and the preservation of the natural zeolite structure, was confirmed through various analyses, including XRD, FESEM, and BET. A strong and favorable correlation was achieved by employing the Box-Behnken design of experiments method to optimize operational parameters, such as adsorbent dosage, initial pollutant concentration, and pH.

From an industrial perspective, the proposed CuO-Fe₃O₄/CP adsorbent offers the following advantages:

1. Cost-effectiveness and scalability: Utilizing

natural CP as a cost-effective substrate significantly reduces total costs compared to fully synthetic nanoparticles. The catalyst's heterogeneous structure ensures the efficient use of active sites and minimizes metal content.

2. Scalable separation: The composite's magnetic properties enable rapid separation from wastewater using an external magnetic field, eliminating the need for complex, energy-intensive high-pressure filtration equipment.

3. Scalability: The adsorbent can be easily integrated into existing treatment lines—using either fixed-bed or stirred-tank reactors—without requiring significant infrastructure modifications.

4. Regeneration and durability: The composite demonstrated high durability over five adsorption-desorption cycles. This characteristic not only reduces the environmental impact associated with sludge generation but also helps minimize operating costs.

Despite the successes achieved in this research, certain limitations regarding the experiments have been identified, notably the challenge of maintaining pollutant stability and the time-consuming nature of concentration measurements. Future research efforts should focus on implementing automated temperature and flow control systems, as well as employing online analysis methods (such as GC-MS). Transitioning from laboratory-scale experiments to a continuous-flow pilot scale will be a crucial step in demonstrating the material's practical applicability.

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CONFLICT OF INTEREST

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

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