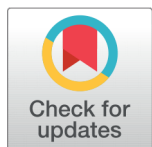


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Adsorptive performance of zinc oxide and iron doped zinc oxide nanoparticles for Cr (VI) removal : Isotherms, Kinetics and Thermodynamics analysis

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Abstract

Objectives: The main objective of this study was to evaluate and compare the adsorption performance of zinc oxide nanoparticles (ZnO NPs) and iron-doped zinc oxide nanoparticles (Fe-ZnO NPs) for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions. **Method:** ZnO NPs and Fe-ZnO NPs were synthesized and characterized using SEM and FTIR analyses to investigate their morphology and surface functional groups. Batch adsorption experiments were conducted under different operating conditions to assess Cr(VI) removal efficiency, adsorption isotherms, kinetics, and thermodynamic behavior. **Findings:** Fe-ZnO NPs exhibited a significantly higher adsorption capacity (166.67 mg g^{-1}) than ZnO NPs (66.67 mg g^{-1}), demonstrating a 2.5-fold enhancement in Cr(VI) removal performance. Adsorption data were best fitted by the Langmuir isotherm model ($R^2 = 0.966\text{--}0.981$), indicating monolayer adsorption, while the pseudo-second-order kinetic model ($R^2 = 0.987\text{--}0.999$) suggested chemisorption as the dominant mechanism. Thermodynamic analysis revealed increased interfacial ordering for Fe-ZnO NPs (negative ΔS°) and increased randomness for ZnO NPs (positive ΔS°). **Novelty:** This study demonstrates that iron doping substantially enhances the Cr(VI) adsorption performance of ZnO NPs and provides a comprehensive understanding of the associated adsorption mechanism. The superior adsorption capacity and favorable adsorption behavior of Fe-ZnO NPs highlight their potential as an efficient adsorbent for the treatment of chromium-contaminated wastewater. **Keywords:** Doped Nanoparticles; Iron Doped Zinc Oxide Nanoparticles; Adsorption; Kinetics; Heavy Metals

1 Introduction

Recent advancements in nanotechnology have established metal oxide nanoparticles as highly promising materials for the efficient removal of toxic heavy metals from contaminated water. Conventional water treatment methods, such as chemical precipitation, coagulation, ion exchange, and membrane filtration, often exhibit limitations including poor efficiency at low metal concentrations, high operational costs, sludge generation, and complex processing requirements^{(1), (2)}. Among various nanomaterials, zinc oxide nanoparticles (ZnO NPs) have attracted considerable attention due to their large surface area, chemical stability, low toxicity, and excellent adsorption performance⁽³⁾. Furthermore, recent studies have revealed that metal doping, particularly iron incorporation into ZnO structures, can significantly enhance surface characteristics, increase active adsorption sites, and improve pollutant removal efficiency⁽⁴⁾.

These advancements have broadened the applicability of ZnO-based nanomaterials for the removal of hazardous contaminants such as hexavalent chromium Cr(VI), a highly toxic and carcinogenic heavy metal commonly discharged from various industrial activities. Although numerous studies have investigated the synthesis and application of ZnO-based nanoadsorbents for heavy metal remediation, most have primarily focused on adsorption efficiency without establishing a comprehensive relationship between structural modifications and adsorption behaviour⁽⁵⁾. In particular, comparative studies evaluating pure ZnO NPs and Fe-ZnO NPs under identical experimental conditions remain limited. Moreover, the influence of iron doping on physicochemical properties, adsorption mechanisms, kinetic and isotherm behaviour, as well as thermodynamic parameters associated with Cr(VI) removal, has not been thoroughly explored⁽⁶⁾. Therefore, the present study focuses on the synthesis and characterization of ZnO NPs and Fe-ZnO NPs, followed by a systematic evaluation of their adsorption performance for the removal of Cr(VI) from aqueous solutions. By integrating recent advancements in nanoparticle modification with detailed adsorption investigations, this study aims to address the existing research gaps and provide deeper insight into the role of iron doping in enhancing the adsorption efficiency of ZnO-based nanoadsorbents for water treatment applications.

2 Methodology

2.1 Chemicals and Reagents

All chemicals and reagents used in this study were of analytical reagent (AR) grade and were used without further purification. Zinc chloride (ZnCl_2 , 98%) was purchased from Central Drug House (P) Ltd.; zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 98%] from Merck Life Science Private Limited; and ferric chloride (FeCl_3 , 98%) and sodium hydroxide (NaOH, 97%) from Loba Chemie Pvt. Ltd. Analytical-grade 2-propanol (isopropyl alcohol) and ethanol were used as received. Deionized water was employed throughout all experimental procedures. A stock solution of Cr(VI) (1000 mg/L) was prepared and subsequently diluted to obtain working solutions of the desired concentrations. The pH of each solution was measured using a digital pH meter and adjusted using 1 N H_2SO_4 or 1 N NaOH. Cr(VI) concentrations were determined using a UV-Visible spectrophotometer.

2.2 Preparation of adsorbents

For synthesizing ZnO NPs, Sodium hydroxide (NaOH, 10 g, 1.0 M) was solubilized in 100 mL distilled water and heated to 50–90 °C with constant stirring. A separate zinc chloride solution (ZnCl_2 , 17 g, 0.5 M in 100 mL water) was then added dropwise over 20–60 min, leading to immediate precipitation, observed by change in colour from colourless to white. After the addition was completed, the mixture was agitated for 2 h at the same temperature and the precipitate were separated from supernatant. The solids were rinsed five times with distilled water (1:10 dilution each time) to remove sodium chloride (NaCl). The washed particles were peptized in 2-propanol using ultrasonication for 10 min at 27 °C, followed through centrifugation at 6,000 rpm for a duration of 15 minutes, filtered, rinsed with deionized water, and desiccated at ≤ 70 °C for several hours⁽⁷⁾. For synthesizing Fe-ZnO NPs, solution A was formulated using 2.2 g of zinc acetate dihydrate and Ferric chloride (FeCl_3) in 160 mL of deionized water, followed by adding 80 mL of ethanol and stirring for 1 h. Solution B (160 mL of 1 M NaOH) was then introduced dropwise to solution A, forming a precipitate that was allowed to settle for two days, filtered, dried which was ultimately calcined at 300 °C for 30 h⁽⁸⁾.

2.3 Adsorption studies

Batch adsorption tests were conducted in a conical flask containing 100 mL of Cr(VI) solution, with pH adjusted using 1 N H_2SO_4 or NaOH. The effect of pH, contact time, adsorbent dose, initial metal ion concentration, temperature was examined.

For pH optimization, the samples were shaken at 150 rpm for 60 minutes at 25 °C across pH 1–10. Adsorbent dosage (10–80 mg) was varied and metal concentration (10–85 mg/L), time (15–120 min) and temperature (15–55 °C) were varied individually. After filtration, Cr(VI) was quantified at 540 nm using a UV–Vis spectrophotometry after forming the diphenylcarbazide complex. Cr(VI) detection was carried out by forming a purple-violet complex with 1,5-diphenylcarbazide under acidic conditions. Each parameter was optimized by varying one factor while keeping all others constant. The equilibrium adsorption capacity (q_e) was calculated using initial and final Cr(VI) concentrations, solution volume, and adsorbent mass, while removal efficiency was determined from the difference between C_i and C_e . These parameters are given by the following equations:

$$\text{Uptake capacity } (q_e) = \frac{C_i - C_e}{m} \times V \quad (1)$$

$$\text{Removal efficiency } (\%) = \frac{C_i - C_e}{m} \times 100 \quad (2)$$

2.4 Adsorption isotherm studies

2.4.1. Langmuir Isotherm Studies

This model accounts for monolayer adsorption onto a homogeneous surface containing a limited number of uniform binding sites, assuming that once a site is saturated, no additional retention can take place at that site and that lateral movement or interaction between adsorbed molecules does not take place⁽⁹⁾. The Langmuir isotherm equation can be written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{qm.K_L} \quad (3)$$

Here, q_e and q_m correspond to the equilibrium and maximum adsorption capacities (mg g^{-1}), respectively. K indicates the Langmuir affinity constant (L mg^{-1}), whereas C_e denotes the residual adsorbate concentration at equilibrium (mg L^{-1}).

2.4.2. Freundlich Isotherm Studies

This isotherm elucidate adsorption on heterogeneous surfaces by incorporating non-uniform distribution of active sites⁽¹⁰⁾. The Freundlich isotherm is expressed as

$$\ln q_e = \frac{1}{n} C_e + \ln K_F \quad (4)$$

In this model, q_e expresses the adsorbed quantity per unit mass (mg g^{-1}), whereas C_e corresponds to the residual concentration at equilibrium, in the liquid phase (mg L^{-1}). The parameters K_F and n describe adsorption capacity and adsorption favorability, respectively.

2.4.3. Temkin Isotherm Studies

In its linear form, the model establishes a relationship between the equilibrium adsorption capacity (q_e) and the equilibrium concentration (C_e)⁽¹¹⁾. The Temkin isotherm equation is given by:

$$q_e = \frac{R_T}{B_T} \ln A_T + \frac{R_T}{B_T} \ln C_e \quad (5)$$

Here, q_e is the equilibrium adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate in solution (mg L^{-1}), A_T denotes the Temkin adsorption constant (L mg^{-1}), B_T represents the Temkin heat-related constant (J mol^{-1}), and R_T corresponds to the product of the gas constant and absolute temperature.

2.5 Kinetics studies

2.5.1. Pseudo-first-order kinetic model

Pseudo-first-order kinetic model (PFO) explains adsorption by relating the rate of solute uptake to time, assuming that the adsorption rate depends on the number of available active sites on the adsorbent surface⁽¹²⁾. The PFO equation is as given as follow:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

Here, q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_t (mg g^{-1}) denotes adsorption at time t , and k_1 (min^{-1}) represents the pseudo-first-order rate constant.

2.5.2. Pseudo- second- order kinetic model

Pseudo- second- order kinetic model (PSO) is a model for describing the adsorption of compounds onto surfaces. This model explains how dissolved ions are adsorbed onto a surface by a chemical mechanism like chemical sharing or cation exchange. It is often used to state how dyes, metal ions, and other compounds adsorb onto adsorbents⁽¹³⁾. This is given by the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_2 t \quad (7)$$

Here, q_e represent the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), q_t depicts the amount of adsorbate adsorbed at time t (mg g^{-1}), k_2 denotes the rate constant of the pseudo-second-order model ($\text{g/mg} \cdot \text{min}$).

2.5.3. Intraparticle diffusion model

The intraparticle diffusion model was used to study the adsorption of arsenic onto zinc oxide nanoparticles, revealing that both surface adsorption and intraparticle diffusion contributed to the overall rate⁽¹⁴⁾. This is given by the following equation:

$$q_t = k_{id} t^{1/2} + C \quad (8)$$

In this relation, k_{id} ($\text{mg g}^{-1} \text{ min}^{-1/2}$) represents the intraparticle diffusion rate constant, while C is a constant associated with the thickness of the boundary layer.

2.6 Thermodynamic Studies

Thermodynamic parameters were evaluated to understand the feasibility and nature of the adsorption process using the Van't Hoff equation⁽¹⁵⁾. From temperature - dependent data, calculations were conducted to ascertain thermodynamic parameters (ΔH° , ΔS° , ΔG°) were computed to assess the spontaneity and nature of Cr(VI) adsorption on and ZnO NPs and Fe-ZnO NPs. The following equations were used for determining various thermodynamics parameters:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

$$K_d = q_e / C_e \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

3 Results and Discussion

3.1 Characterization studies of ZnO NPs and Fe-ZnO NPs

3.1.1. FT-IR studies

The FTIR spectra of the synthesized nanoparticles exhibited a broad band around 3400 cm^{-1} and an absorption near 1600 cm^{-1} , corresponding to the stretching and bending vibrations of hydroxyl groups and adsorbed water molecules. Weak bands in the $1400\text{--}1000 \text{ cm}^{-1}$ region were attributed to C–O and/or C–N stretching vibrations (Figure 1). The most prominent absorption features were observed in the low-wavenumber region, where strong metal–oxygen vibrations confirmed nanoparticle formation. ZnO NPs exhibited characteristic Zn–O stretching vibrations in the $500\text{--}430 \text{ cm}^{-1}$ region, while Fe-ZnO NPs showed slight shifts in these bands, indicating successful iron incorporation into the ZnO lattice. Similar spectral shifts have been reported for Fe-doped ZnO nanoparticles and were attributed to lattice distortion and changes in the local bonding environment caused by dopant incorporation^{(16), (17)}.

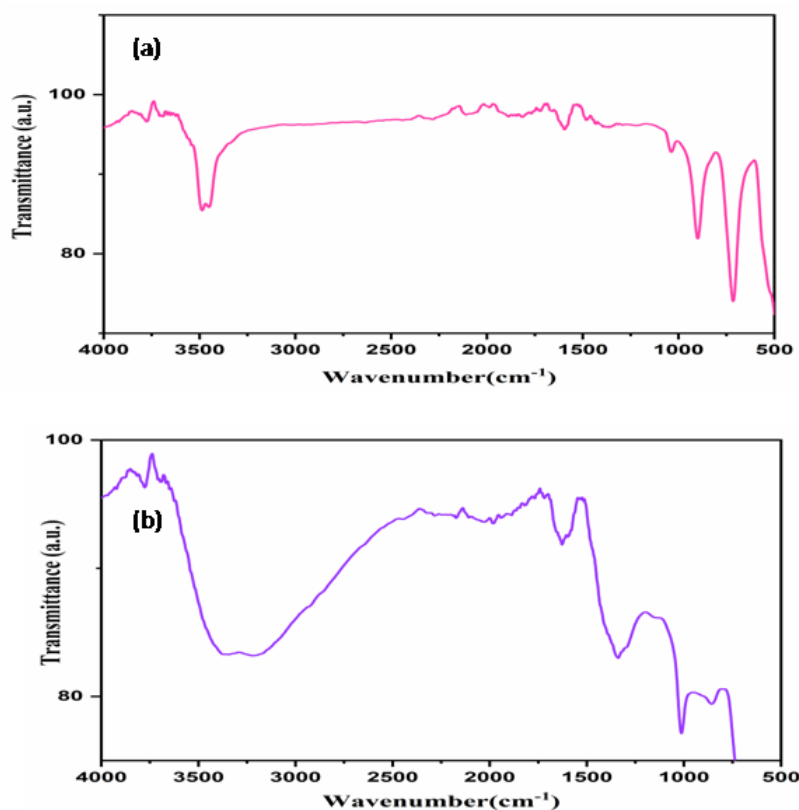


Fig 1. FTIR analysis of (a) ZnO NPs, (b) Fe-ZnO NPs

3.1.2. Scanning Electron Microscopy (SEM) studies

ZnO NPs exhibited well-defined hexagonal and plate-like nanosheets forming flower-like aggregates, characteristic of the wurtzite ZnO structure. Fe-ZnO NPs exhibited sheet-like and flower-shaped aggregates similar to those of ZnO NPs; however, the incorporation of Fe^{3+} ions introduced noticeable distortions and irregularities in the crystal morphology (Figure 2). This modification disrupted the typical ZnO NPs growth pattern, resulting in increased surface roughness and structural defects, which are advantageous for improving adsorption efficiency during heavy metal removal. SEM analysis of ZnO NPs revealed the presence of pores between aggregated nanoparticles, with the structures displaying predominantly oval and spherical shapes. These changes indicate the influence of Fe incorporation on nanoparticle growth and surface characteristics. The resulting increase in surface roughness and accessibility of adsorption sites is expected to enhance the interaction between the adsorbent surface and Cr(VI) ions, leading to improved adsorption performance⁽¹⁸⁾.

3.2 Adsorption dynamics

3.2.1. Effect of pH

pH is a crucial factor governing the adsorption of Cr(VI), as it strongly influences the surface charge and availability of binding sites on the adsorbent, as well as the speciation of chromium ions in solution. Cr(VI) exists in several anionic forms in aqueous media, including chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and hydrogen chromate (HCrO_4^-)⁽¹⁹⁾. pH showed a crucial role in regulating Cr(VI) adsorption. Its influence was evaluated by adjusting the pH from 1 to 10 under fixed conditions, 30 mg adsorbent dose, 50 mg/L initial metal ion concentration, 60 minutes contact time, and 25 °C (Figure 3). The pH-dependent Cr(VI) removal by ZnO NPs and Fe-ZnO NPs showed maximum efficiency under acidic conditions due to strong electrostatic attraction between positively charged adsorbent surfaces and negatively charged chromate ions. The observed pH-dependent adsorption behavior agrees with literature findings, where Cr(VI) removal efficiency was highest under acidic conditions and decreased with increasing pH. This trend has been attributed to the protonation of adsorption sites and stronger electrostatic

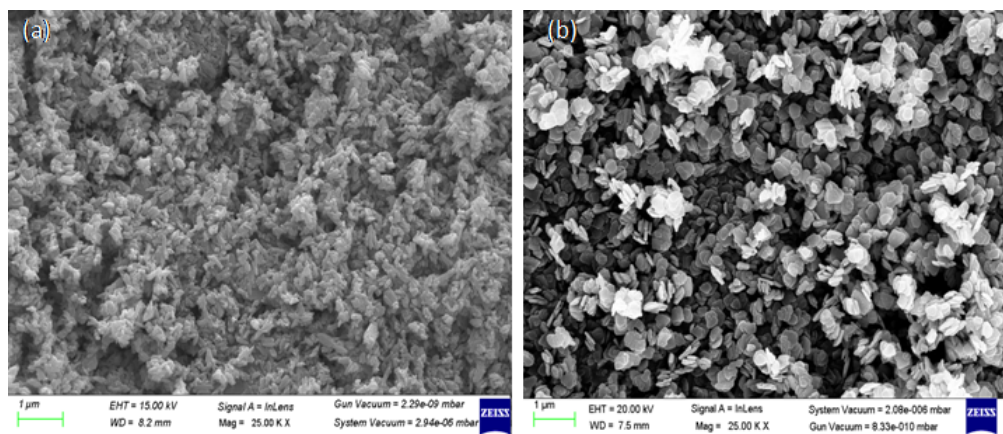


Fig 2. Surface morphology of (a) ZnO NPs, (b) Fe-ZnO NPs

attraction between the adsorbent surface and anionic chromium species at lower pH values, whereas reduced surface reactivity at higher pH limits Cr(VI) uptake^{(20), (21)}.

3.2.2. Effect of Adsorbent Dose

The adsorbent dose effect was examined by varying the amount of ZnO NPs and Fe-ZnO NPs from 10–80 mg, while maintaining constant conditions of pH 2, initial Cr(VI) concentration of 50 mg L⁻¹, contact time of 60 min, and temperature of 25 °C. The Cr(VI) removal efficiency was found to be maximum of 76.64% using 70 mg dosage of ZnO NPs and 82.46% using 40 mg dosage of Fe-ZnO NPs (Figure 3). These findings indicated that these adsorbents achieve substantial heavy metal removal even at relatively low dosage levels. The removal efficiency increased sharply with increasing adsorbent dose up to an optimum point, after which the curve begins to slightly decrease. At lower dosage the removal was relatively low due to insufficient active sites. Fe-ZnO NPs exhibited the highest removal, reaching about 80–82% removal, followed by ZnO NPs. Beyond the optimum dose, the curves flattened because the system reached near saturation and excess adsorbent caused particle aggregation, reducing effective surface area. Overall, Fe-ZnO NPs demonstrated superior adsorption due to the combined surface reactivity of iron and zinc oxide. The removal efficiency generally increases with increasing adsorbent dosage due to the greater availability of active adsorption sites and enhanced surface area for metal ion uptake. However, beyond the optimum dosage, the improvement in removal efficiency becomes negligible or may slightly decrease because of particle aggregation, overlap of adsorption sites, and reduced effective surface area⁽²²⁾.

3.2.3. Effect of Contact Time

The study was conducted by varying contact time from 5 to 120 minutes intervals, while keeping pH 2, adsorbent dosage (40 mg and 70 mg for Fe-ZnO NPs and ZnO NPs respectively), initial metal ion concentration (50 mg/L), and temperature (25 °C) constant. Removal efficiency of Cr(VI) increased over time and reached equilibrium, achieving 83.86 % for Fe-ZnO NPs at 45 minutes and 70.85% for ZnO NPs at 30 minutes (Figure 3). A fast rise in removal efficiency through the initial contact period, followed by attainment of maximum adsorption, and then a slight decline at longer times. At the beginning adsorption increases sharply because plenty of vacant active sites were available on the nanoparticle surfaces, thereafter starts declining slowly. After the optimum time, the removal efficiency of Cr(VI) declines gradually due to desorption, saturation of sites, or re-release of loosely bound Cr(VI) back into the solution. Rapid initial adsorption of Cr(VI), followed by attainment of equilibrium within 30–60 min, has been reported for ZnO-based nanoadsorbents, which is attributed to the progressive occupation of available active sites on the adsorbent surface⁽²³⁾.

3.2.4. Effect of Initial Metal Ion Concentration

The influence of initial Cr(VI) concentration evaluated by increasing it from 15 to 85 mg/L under fixed conditions viz. pH 2 for both adsorbents, adsorbent dosage of 70 mg and 40 mg for ZnO NPs and Fe-ZnO NPs, contact time of 30 minutes for ZnO NPs and 40 minutes for Fe-ZnO NPs, and 25 °C temperature. The removal efficiency progressively declined due to saturation of active sites and increased competition among chromium ions, leaving more ions unadsorbed. The drop was most pronounced in ZnO NPs and moderate in Fe-ZnO NPs (Figure 3). At higher concentrations, the number of chromium ions exceeds the

available adsorption sites, resulting in site saturation and greater competition among ions for binding sites. Modified ZnO NPs generally exhibit a less pronounced decline in removal efficiency due to their higher surface area and greater number of active adsorption sites⁽²⁴⁾.

3.2.5. Effect of Temperature

Temperature was varied from 15 to 55 °C under constant conditions viz. pH 2 for both adsorbent, adsorbent dosage of 70 mg of ZnO NPs and and 40 g of Fe-ZnO NPs, and 50 mg/L initial metal ion concentration. Removal efficiency increased with temperature, reaching maximum of 85 % for ZnO NPs at 35 °C , 92.25 % for Fe-ZnO NPs at 45 °C (Figure 3). Higher temperatures enhance the mobility of Cr(VI) ions and facilitate their interaction with active adsorption sites, resulting in improved removal efficiency⁽²⁵⁾.

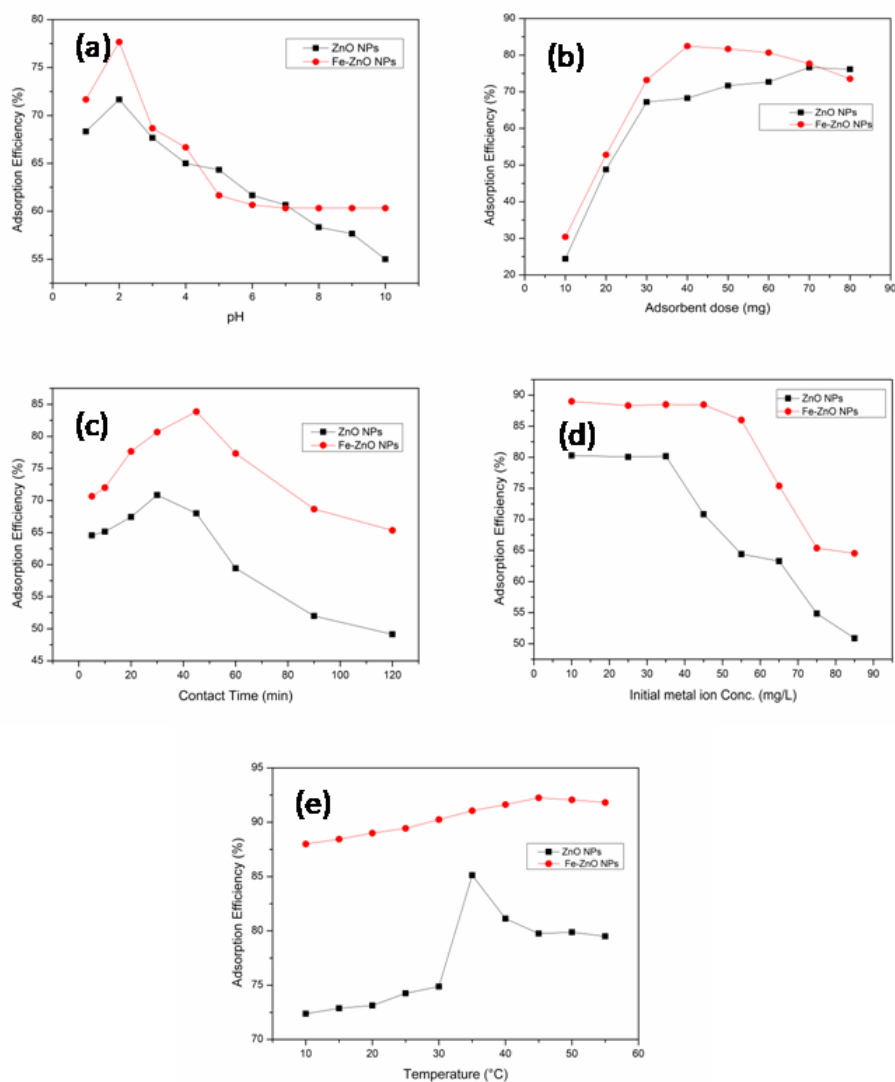


Fig 3. Influence of (a) pH, (b) adsorbent dose, (c) contact time, (d) initial metal ion conc. , (e) temperature on Cr(VI) adsorption using ZnO NPs and Fe-ZnO NPs

3.3 Isotherm Studies

The isotherm results showed that Fe-ZnO NPs more adsorption affinity and capacity for Cr(VI) than ZnO NPs (Table 1). The Langmuir data indicated a maximum monolayer adsorption capacity (Q_m) of 166.67 mg g^{-1} for Fe-ZnO NPs, which was significantly higher than ZnO NPs (66.67 mg g^{-1}), confirming that doped NPs provided more active sites and stronger surface interactions (Figure 4). The Langmuir R^2 values (0.966–0.981) suggested that adsorption was largely monolayer and favors chemisorption, while the R_L values (<1) confirmed the process to be favorable for both adsorbents provided these constants⁽²⁶⁾. Fe-ZnO NPs showed a good balance of heterogeneity and capacity ($n = 1.9$). It had been showed that ZnO NPs had moderate heat of adsorption and Fe-ZnO NPs had slightly higher BT, suggesting stronger adsorbate–adsorbent interactions.

Table 1. Isotherm derived parameters for Cr(VI) adsorption on ZnO NPs and Fe-ZnO NPs

Isotherm	Parameters	ZnO NPs	Fe-ZnO NPs
Langmuir	$q_m \text{ (mg g}^{-1}\text{)}$	66.67	166.67
	B	0.0857	0.1935
	R^2	0.9	0.966
	R_L	0.189	0.0937
Freundlich	N	1.83	1.898
	$K_F \text{ (L/g)}$	10.39	30.7
	R^2	0.89	0.802
Temkin	$B_T \text{ (KJ/mol)}$	0.147	0.074
	$A_T \text{ (g/L)}$	1.143	2.52
	R^2	0.97	0.872

3.4 Kinetic Studies

The kinetic parameters clearly indicated that PSO kinetics best described adsorption on these nanoparticles, as shown by the very high R^2 values (0.987–0.999) compared to PFO confirming that the adsorption process was predominantly chemisorption involving valence forces and electron sharing/exchange as summarized in Table-2. The linear form was plotted as t/q_t versus t (Figure 9), and k_2 and q_e were calculated from the slope and intercept. Fe-ZnO NPs showed fast adsorption ($K_2 = 0.012 \text{ g/mg/min}$) with a q_e close to the experimental value indicating greater active site availability. The model shows that diffusion is responsible for adsorption but is not the only rate-controlling step, as indicated by the nonzero intercepts (X_i) and R^2 values <1 . Fe-ZnO NPs performed best with high K_i ($3.449 \text{ mg g}^{-1} \cdot \text{min}^{0.5}$) and strong correlation ($R^2 = 0.979$), suggesting faster internal diffusion compared to undoped NPs (Figure 5). Recent studies on ZnO NPs have also shown that Cr(VI) adsorption is adequately described by the pseudo-second-order kinetic model, suggesting that chemisorption plays a significant role in the adsorption process. The contribution of intraparticle diffusion, together with surface adsorption, indicates that multiple mechanisms govern Cr(VI) uptake by ZnO-based adsorbents⁽²⁷⁾.

3.5 Thermodynamics studies

Fe-ZnO NPs showed a positive enthalpy change ($\Delta H^\circ = +25.6 \text{ kJ/mol}$), indicating that its adsorption of Cr(VI) was endothermic, meaning higher temperatures favored adsorption, whereas ZnO NPs ($\Delta H^\circ = -2.469 \text{ kJ/mol}$) exhibited exothermic adsorption, became less favorable at elevated temperatures. Van't Hoff graphs were plotted depicting the suitability of ZnO NPs over Fe-ZnO NPs for Cr(VI) removal (Figure 6). The negative entropy values for Fe-ZnO NPs ($\Delta S^\circ = -55.9$) indicates increased order at the solid–solution boundary during adsorption, while ZnO NPs shows a positive ΔS° , indicated increased randomness (Table-3). The effect of temperature observed in the present study is comparable to that reported by studies where the adsorption of Cr(VI) exhibited temperature-dependent behavior and was found to be thermodynamically favorable within a specific temperature range⁽²⁸⁾.

3.6 Comparative Assessment

A comparative assessment of previously reported ZnO-based nanoadsorbents for Cr(VI) removal indicates that adsorption behavior is predominantly described by the Langmuir isotherm and pseudo-second-order kinetic models, suggesting

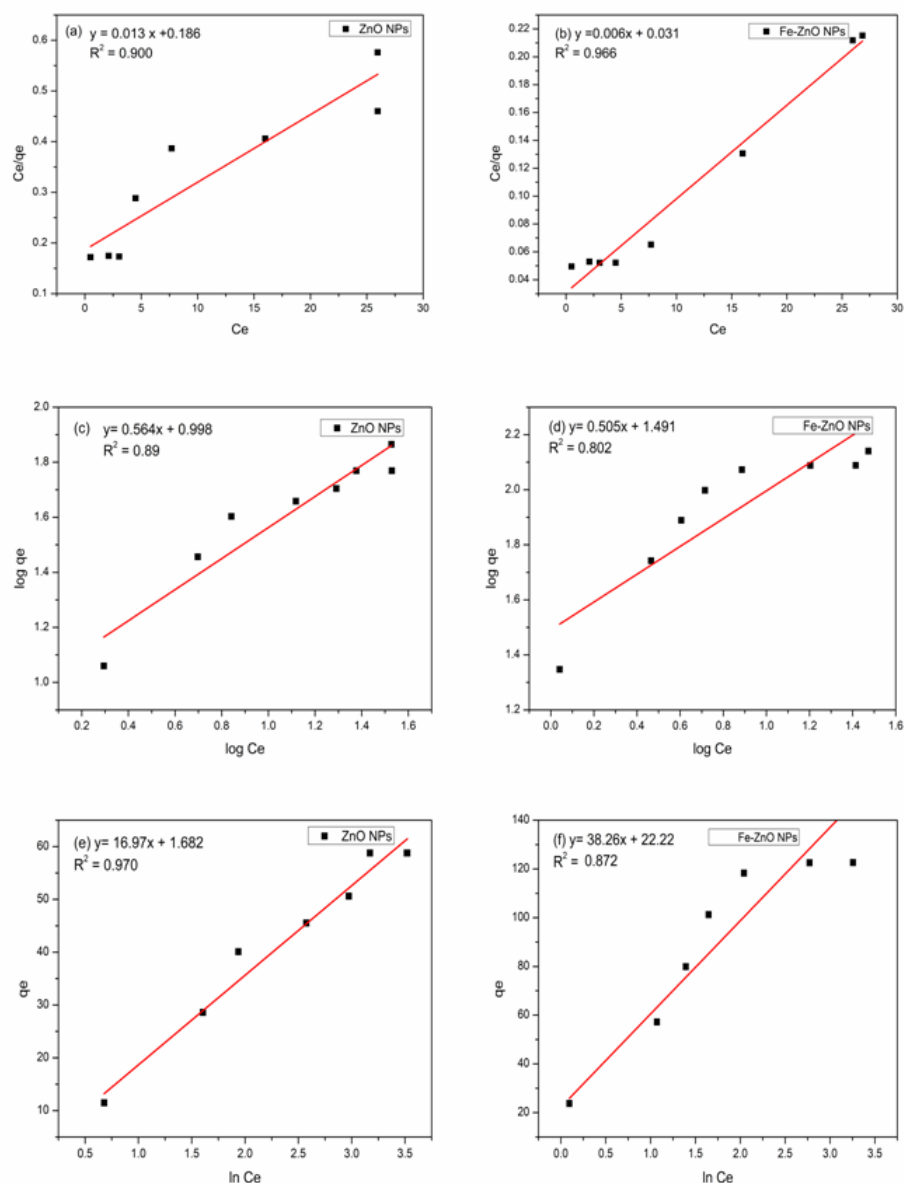


Fig 4. Isotherm analysis of Cr(VI) adsorption onto ZnO NPs and ZnO NPs: (a), (b) Langmuir isotherm; (c), (d) Freundlich isotherm; (e), (f) Temkin isotherm

monolayer adsorption and chemisorption as the principal removal mechanisms. As summarized in Table 4, the reported adsorption capacities vary considerably depending on the synthesis route and material modification, ranging from 1.81 mg g⁻¹ for AC/ZnO nanocomposites to 68.00 mg g⁻¹ for green-synthesized ZnO NPs. Although several modified ZnO systems, including GO-ZnO, Ag/ZnO-activated carbon, rGO-ZnO, and C-ZnO nanocomposites, have demonstrated enhanced adsorption performance, many studies have reported moderate adsorption capacities and limitations such as insufficient thermodynamic evaluation, multi-step synthesis procedures, or inadequate regeneration studies. In the present study, pure ZnO NPs exhibited an adsorption capacity of 66.67 mg g⁻¹, comparable to the highest values reported in the literature. More importantly, Fe-ZnO NPs nanoparticles achieved a substantially higher adsorption capacity of 166.67 mg g⁻¹, exceeding all previously reported ZnO-based adsorbents included in Table 4. Both ZnO NPs and Fe-ZnO NPs followed the Langmuir

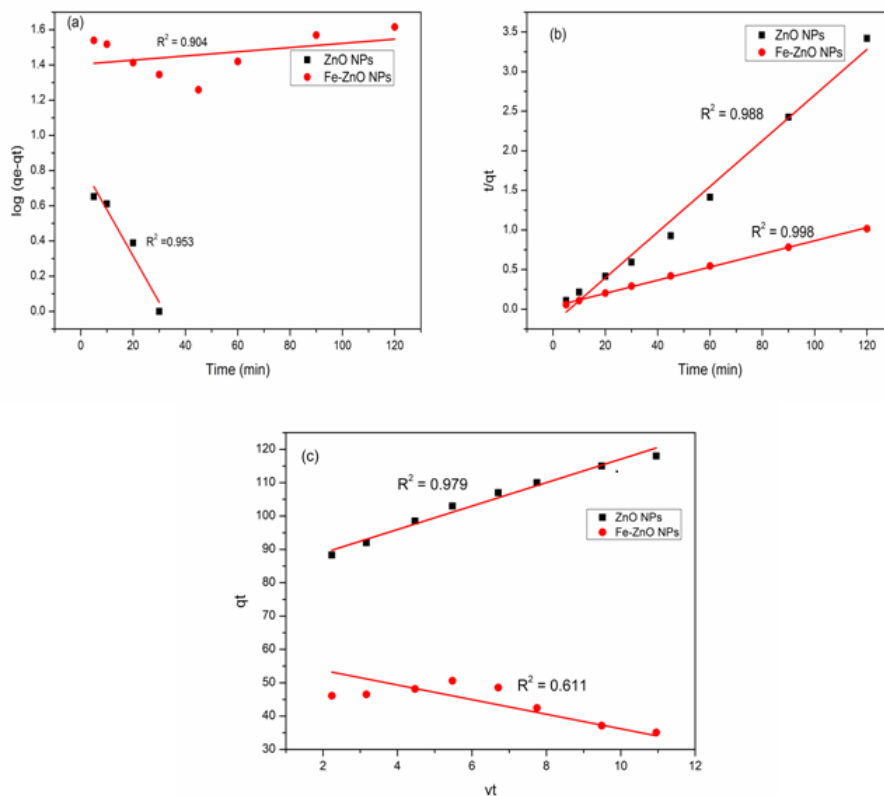


Fig 5. Kinetic behavior of Cr(VI) adsorption onto ZnO NPs and Fe-ZnO NPs: (a) PFO, (b) PSO, and (c) intra-particle diffusion model

Table 2. Kinetic Model parameters for Cr(VI) adsorption on ZnO NPs and Fe-ZnO NPs

Kinetics model	ZnO NPs	Fe-ZnO NPs
PFO kinetics Model		
q_e cal (mg g^{-1})	6.92	31.33
K_1 (1/min)	0.0599	0.00691
R^2	0.953	0.904
PSO kinetics Model		
q_e cal (mg g^{-1})(g/mg/min)	35.71	30.3
K_2 (g/mg/min)	0.987	0.012
R^2	0.988	0.998
Intra-particle diffusion Model		
K_i ($\text{mg g}^{-1} \text{ min}^{0.5}$)	1.123	3.449 mg g^{-1}
X_i (mg g^{-1})	33.45	82.31 mg g^{-1}
R^2	0.611	0.979

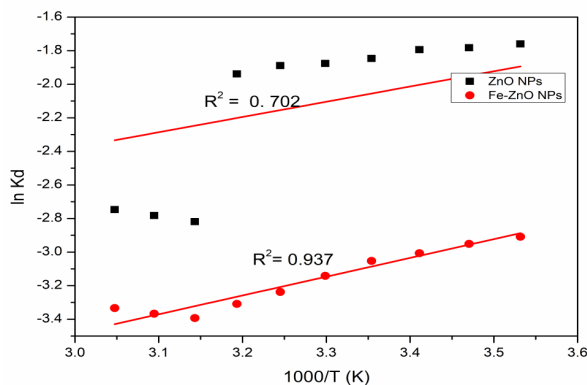


Fig 6. Van't Hoff for of Cr(VI) adsorption onto ZnO NPs and Fe-ZnO NPs

Table 3. Thermodynamic characteristics of Cr(VI) adsorption onto ZnO NPs and Fe-ZnO NPs

Thermodynamics parameters					
Adsorbents	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)	ΔG° (KJ/mol)		
ZnO NPs	-2.469	32.52	T (in Kelvin)		
			303.15	ZnO NPs	Fe-ZnO NPs
			308.15	-12.327	+42.53
				-12.489	+42.82
Fe-ZnO NPs	25.6	-55.9	283.15	-11.676	+41.42
			288.15	-11.83	+41.71

isotherm and pseudo-second-order kinetic models, indicating favorable monolayer adsorption governed by chemisorption. The remarkable enhancement in adsorption performance following iron doping can be attributed to the increased availability of active adsorption sites and stronger interactions between Cr(VI) species and the adsorbent surface. These findings demonstrate the effectiveness of Fe-ZnO NPs as a highly promising adsorbent for Cr(VI) remediation and highlight the beneficial role of iron incorporation in improving ZnO-based adsorption systems.

Fe-ZnO NPs demonstrate considerable potential for practical wastewater treatment applications due to their high Cr(VI) adsorption capacity (166.67 mg g^{-1}), which was significantly greater than that of pure ZnO NPs. The enhanced adsorption performance achieved through iron doping suggests that these nanoparticles can serve as efficient adsorbents for the treatment of chromium-contaminated effluents generated by electroplating, leather tanning, metal finishing, and pigment industries. Compared with many conventional adsorbents, Fe-ZnO NPs offer advantages such as high adsorption efficiency, relatively simple synthesis, and the use of readily available materials. Furthermore, their ability to effectively remove toxic Cr(VI) from aqueous systems highlights their relevance for environmental remediation and water quality improvement. Although the present results demonstrate strong potential for practical application, further studies on regeneration, reusability, cost analysis, and pilot-scale operation are required to assess the feasibility of large-scale implementation and long-term sustainability.

4 Conclusion

The successful synthesis of ZnO NPs and Fe-ZnO NPs was confirmed through SEM and FTIR analyses, which revealed uniformly distributed nanosized particles, enhanced surface roughness after iron doping, and characteristic metal-oxygen vibrations responsible for adsorption activity. Adsorption studies demonstrated that Fe-ZnO NPs exhibited comparatively higher Cr(VI) removal efficiency than pure ZnO NPs, confirming the positive effect of iron incorporation on adsorption performance. Thermodynamic analysis further revealed negative entropy (ΔS°) values for Fe-ZnO NPs, indicating increased interfacial ordering during adsorption, whereas ZnO NPs showed positive entropy (ΔS°) values suggesting greater randomness at the solid-solution interface. The present work's novelty is the systematic comparison of ZnO NPs and Fe-ZnO NPs through combined structural, spectral, kinetic, isotherm, and thermodynamic analyses under identical experimental conditions. Overall, the results confirm that Fe-ZnO NPs have superior surface characteristics and stronger affinity towards Cr(VI) adsorption compared to pure ZnO NPs. Future studies should concentrate on regeneration and reusability assessment,

Table 4. Comparative Performance of Zinc oxide based nanodisorbents for Cr(VI) removal

Nanomaterial	Synthesis Method	Best Fit Model	Adsorption Capacity (mg g^{-1})	Key Finding / Limitation	Ref-er-ence
ZnO nanoparticles	Plant-mediated synthesis	Langmuir; Pseudo-second-order	68.00	Good Cr(VI) adsorption performance; thermodynamics not reported	(29)
Activated Carbon/ZnO (AC/ZnO) nanocomposite	Composite synthesis	Langmuir; Pseudo-second-order	1.81	Activated carbon improved adsorption; low adsorption capacity	(30)
Graphene Oxide–ZnO (GO–ZnO) nanohybrid	Solvothermal synthesis	Langmuir; Pseudo-second-order	3.69	Effective adsorption at near-neutral pH; limited adsorption capacity	(31)
Silver/ZnO–Activated Carbon (Ag/ZnO–AC) nanocomposite	Green synthesis	Freundlich; Pseudo-second-order	4.17	Eco-friendly adsorbent; moderate adsorption performance	(32)
Onion peel extract-mediated ZnO nanoparticles (ZnO–O)	Green synthesis using onion peel extract	Freundlich; Pseudo-second-order	20.74	Improved adsorption and reusability; moderate adsorption capacity	(33)
Reduced Graphene Oxide–ZnO (rGO–ZnO) nanocomposite	Chemical reduction + ZnO incorporation	Langmuir; Pseudo-first-order	25.45	Higher adsorption than GO; multi-step synthesis process	(34)
Carbon-doped ZnO (C–ZnO) nanoparticles	Green synthesis using <i>Lantana camara</i> seed extract	Langmuir; Pseudo-second-order	34.84	Reusable for multiple cycles; capacity lower than doped systems	(35)
ZnO nanoparticles	Chemical synthesis	Langmuir; Pseudo-second-order	66.67	Comprehensive adsorption, kinetic and thermodynamic evaluation; regeneration not investigated	[This Study]
Fe–ZnO nanoparticles	Iron-doped ZnO synthesis	Langmuir; Pseudo-second-order	166.67	Highest adsorption capacity; Fe doping enhanced Cr(VI) removal; long-term stability requires investigation	[This Study]

real wastewater treatment, and doping concentration optimisation to further enhance adsorption efficiency and practical applicability. The systematic comparison of ZnO NPs and Fe-ZnO NPs using combined structural, spectral, kinetic, isotherm, and thermodynamic analyses under comparable experimental conditions is what makes this work novel. Overall, the findings verify that, in comparison to pure ZnO NPs, Fe-ZnO NPs have better surface properties and a greater affinity for Cr(VI) adsorption. To further increase adsorption efficiency future research should concentrate on doping concentration optimization and practical applicability.

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