

Facile Synthesis of Magnetic ZIF-67@Fe₃O₄ Composite with Synergistic Properties for Monolayer Adsorption of Pb(II) Pollutants

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Abstract

The development of efficient and easily recoverable adsorbents for heavy metal removal remains a significant challenge in wastewater treatment. In this study, a magnetic ZIF-67@Fe₃O₄ (ZIFO) composite was successfully synthesized via a simple methanol-assisted in situ method at ambient temperature for the removal of Pb(II) from aqueous solution. The physicochemical properties of the synthesized material were comprehensively characterized using XRD, FTIR, FESEM-EDS, HR-TEM, Raman spectroscopy, BET surface area analysis, and XPS, Zeta potential, confirming the successful integration of Fe₃O₄ into the ZIF-67 framework. Batch adsorption experiments were conducted to evaluate the effects of pH, contact time, and initial Pb(II) concentration on adsorption performance. The results showed that Pb(II) uptake was strongly dependent on solution pH, with optimal removal achieved at pH 6. Under the optimized conditions, ZIFO exhibited an experimental adsorption capacity of 212.69 mg g⁻¹ and achieved up to 99.86% Pb(II) removal. Kinetic analysis revealed that the adsorption process was best described by the pseudo-second-order model (R² = 0.99535), indicating that chemisorption dominated the adsorption mechanism. The equilibrium data were well-fitted by the Langmuir isotherm model (R² = 0.9887), with a maximum monolayer adsorption capacity of 158.73 mg g⁻¹. These findings demonstrate that ZIFO is a fast, efficient, and magnetically separable adsorbent with strong potential for the practical treatment of Pb(II)-contaminated wastewater.

Keywords

Adsorption, Fe₃O₄, Pb(II), ZIF-67, ZIF-67@Fe₃O₄

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1. INTRODUCTION

In recent decades, the rapid advancement of science and technology has accelerated industrial development, while simultaneously intensifying pressure on environmental quality and human health (Wen et al., 2017; Saxena, 2025; Jiang et al., 2023). Among the various contaminants released into aquatic systems, heavy metals have become one of the most serious threats due to their persistence, toxicity, and tendency to accumulate in living organisms. Lead (Pb(II)), in particular, is a highly toxic heavy metal widely used in strategic industrial sectors such as battery manufacturing, rubber processing, fossil fuel production, and pesticides. Even at low concentrations, Pb(II) exposure can cause irreversible physiological damage to humans and aquatic organisms through bioaccumulation and biomagnification along the food chain (Moghadam et al., 2021).

Heavy metal contamination in water systems has therefore become an urgent global issue because of the non-biodegradable nature of metal ions and their strong affinity for essential biological macromolecules (Zaynab et al., 2022; Sall et al., 2020; Paithankar et al., 2021). To address this problem, considerable efforts have been devoted to developing effective technologies for the remediation of Pb(II)-contaminated wastewater. Various physicochemical methods have been investigated, including biological oxidation (Kumar et al., 2021), adsorption (Nazir et al., 2022; Fu et al., 2022; Tu et al., 2018), photocatalysis (Maryanti et al., 2025), chemical coagulation (Akinawo et al., 2023), and ion exchange (Baker et al., 2009). Among these approaches, adsorption using porous materials is considered one of the most promising strategies because of its high removal efficiency, simple operation, economic feasibility, and adaptability in water treatment processes. However, conven-

tional adsorbents such as fly ash, commercial activated carbon (Bandura et al., 2021), mesoporous activated carbon (Zhu et al., 2023), chitin hydrogel beads impregnated with nonionic or anionic surfactants (Khoshkho et al., 2021), spinel CoFe_2O_4 (Liaskovska et al., 2025), and natural zeolite modified with N,N-dimethyl dehydroabietylamine oxide (Liu et al., 2018) often suffer from limited adsorption capacity, low selectivity, and poor regeneration performance, thereby restricting their large-scale practical application. Consequently, the development of advanced adsorbents with high specific surface area, abundant active sites, and strong affinity toward Pb(II) remains a key challenge in environmental materials science.

Metal–Organic Frameworks (MOFs) have emerged as highly attractive materials for pollutant removal owing to their crystalline porous structures, exceptionally high surface areas, and tunable metal active sites (Yuan et al., 2018). Recent studies have shown that the performance of MOFs can be further improved through hybridization or composite formation with other functional materials, such as $\text{CsPbBr}_3/\text{Ce-MOF}/\text{SiO}_2$ nanocomposites (Ren et al., 2022), $\text{Fe}_3\text{O}_4\text{-COOH}/\text{H-ZIF-67}$ (Chen et al., 2024a), polystyrene/MOF composites (Kumar et al., 2025), $\text{Fe}_3\text{O}_4/\text{microporous MOFs}$ (Ke et al., 2019), and $\text{UiO-66}/\text{CTS}$ aerogels (Yang et al., 2021). These hybrid systems often exhibit enhanced structural stability, improved adsorption efficiency, and multifunctional properties that are beneficial for environmental remediation.

Among the various MOF families, Zeolitic Imidazolate Framework-67 (ZIF-67), constructed from cobalt ions and 2-methylimidazole ligands, has attracted significant attention because of its excellent thermal stability, chemical robustness, and good performance in aqueous environments (Ma et al., 2020). As a result, ZIF-67 has been widely explored in catalysis (Bavykina et al., 2020; Konnerth et al., 2020; Maryanti et al., 2025), adsorption (Tu et al., 2018; Zhao et al., 2018; Zhang et al., 2016), gas storage (Jia et al., 2022), chemical sensing (Matatagui et al., 2018), and biomedical applications such as drug delivery (Ren et al., 2022). More importantly, recent studies indicate that the physicochemical performance of ZIF-67 can be significantly enhanced through the formation of composites with other functional materials. For instance, $\text{HNTs}/\text{ZIF-67}$, prepared through the in-situ growth of ZIF-67 on halloysite nanotubes, was reported as an efficient heterogeneous catalyst for the Knoevenagel condensation reaction with a catalytic activity of 99% (Hou and Wu, 2020). Wei et al. (2022) modified the surface charge of ZIF-67 using phosphotungstic acid and obtained an adsorbent with an adsorption capacity of 446.4 mg g^{-1} for methylene blue. Maryanti et al. (2025) synthesized $\text{ZIF-67}/\text{SiO}_2$ as a catalyst for Congo red degradation, achieving a removal efficiency of 72.79%.

Despite these advantages, the practical use of powdered ZIF-67 remains limited by the difficulty of separating fine particles from aqueous media after treatment, which may result in material loss and even secondary pollution. Incorporating magnetic nanoparticles into the MOFs structure offers an effective strategy to overcome this limitation by enabling rapid mag-

netic recovery while potentially generating synergistic effects that enhance adsorption performance. Previous studies have demonstrated that $\text{Fe}_3\text{O}_4/\text{MnO}_2(310)/\text{ZIF-67}$ exhibited a remarkably high adsorption capacity toward Cu^{2+} ($1261.60 \text{ mg g}^{-1}$), attributed to the synergistic interaction between MnO_2 and ZIF-67 (Wang et al., 2023). Nazir et al. (2021) reported the combination of Fe with ZIF-67 for RhB removal, achieving a degradation efficiency of 79.92%. $\text{Fe}_3\text{O}_4/\text{ZIF-67}$ has also been employed as a heterogeneous catalyst for the rapid degradation of tetrabromobisphenol A (TBBPA), with 93.4% efficiency within 10 min (Chen et al., 2021). In another study, Song et al. (2022) synthesized $\text{Fe}_3\text{O}_4/\text{ZIF-8}/\text{ZIF-67}$ for tetracycline removal from water, reaching a removal efficiency of more than 95.47%. These findings confirm that magnetic ZIF-based composites exhibit strong magnetic responsiveness and improved functionality, making them highly attractive for post-treatment separation and wastewater purification.

Nevertheless, although numerous studies have reported ZIF-67-based hybrid materials for the removal of organic pollutants, the application of magnetic ZIF-67 composites specifically integrated with Fe_3O_4 nanoparticles for Pb(II) removal remains insufficiently explored. In recent years, the integration of magnetic iron oxide nanoparticles (Fe_3O_4) with zeolitic imidazolate frameworks, particularly ZIF-67, has attracted considerable attention as an effective strategy for developing advanced adsorbents for environmental remediation. These magnetic metal–organic framework (M-MOF) composites combine the tunable porosity and abundant coordination sites of ZIF-67 with the magnetic responsiveness of Fe_3O_4 , enabling efficient adsorbate interaction and facile post-treatment separation, thereby overcoming the recovery limitations commonly associated with conventional MOF powders (Omer et al., 2021). Consequently, various fabrication approaches, including solvothermal, hydrothermal, and in-situ growth methods, have been explored to construct $\text{Fe}_3\text{O}_4/\text{ZIF-67}$ -based composites for the removal of hazardous aquatic pollutants.

Despite significant progress, many reported synthesis strategies still rely on elevated temperatures, extended reaction durations, and organic solvents or stabilizing agents, which may increase production costs and environmental impacts. Moreover, conventional synthesis routes commonly generate ZIF-67 structures with typical polyhedral or rhombic dodecahedral morphologies, where limited exposure of specific active facets may influence adsorption interactions with target pollutants. Therefore, developing a simple, sustainable, and controllable synthesis approach for constructing $\text{Fe}_3\text{O}_4/\text{ZIF-67}$ composites with enhanced surface chemical activity and efficient pollutant removal capability remains an important research objective. To position the present work within the current development of ZIF-67-based magnetic adsorbents, a comparative analysis of reported synthesis methods, structural characteristics, and morphologies of representative ZIF-67 and Fe_3O_4 -containing composites is summarized in Table 1.

As summarized in Table 1, most previously reported ZIF-67 and $\text{Fe}_3\text{O}_4/\text{ZIF-67}$ composites exhibit conventional polyhe-

dral morphologies obtained through solvothermal, hydrothermal, or post-modification strategies. In this work, we demonstrate a facile synthesis approach for a magnetic ZIF-67@Fe₃O₄ (ZIFO) composite. This structural evolution provides improved accessibility of adsorption sites and facilitates mass transport during heavy metal removal. The synthesized ZIFO composite demonstrates excellent Pb(II) adsorption performance, achieving an experimental adsorption capacity (q_e (exp)) of 212.69 mg g⁻¹, which is competitive with or superior to many previously reported ZIF-67-based adsorbents under comparable conditions. In addition, the incorporation of Fe₃O₄ provides magnetic recoverability, improving the practical applicability of the composite for wastewater treatment. This study therefore offers a sustainable strategy for designing high-performance magnetic MOF-based adsorbents for toxic heavy metal remediation.

Therefore, in this study, a magnetic ZIF-67@Fe₃O₄ (ZIFO) composite was successfully synthesized through a facile in situ method at room temperature using methanol as the solvent medium. The physicochemical properties of the resulting ZIFO heterostructure were comprehensively characterized using FTIR, XRD, FESEM-EDS, HR-TEM, Raman spectroscopy, XPS, zeta potential, and BET surface area analysis. Its adsorption behavior toward Pb(II), as well as the residual Pb(II) concentration after treatment, was quantitatively evaluated using Atomic Absorption Spectrophotometry (AAS). The synthesized ZIFO composite is expected to exhibit high Pb(II) adsorption capacity together with rapid magnetic separability, thereby offering a promising and sustainable adsorbent for practical heavy metal remediation in aqueous systems.

2. EXPERIMENTAL SECTION

2.1 Materials

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, ≥99.5%), methanol, and ethanol were purchased from Merck, Germany. 2-Methylimidazole (2-MeIm, ≥98%) and Pb(II) precursor were obtained from Sigma-Aldrich, Germany. Hydrochloric acid (37%) and ammonium hydroxide (33%) were also supplied by Sigma-Aldrich, Germany. Fe₃O₄ was synthesized from iron sand. Whatman No. 42 filter paper (Hyundai) and distilled water (Brataco) were used throughout the experiments. All chemicals and solvents employed in this study were of analytical grade and used without further purification.

2.2 Methods

2.2.1 Synthesis of Fe₃O₄ Nanoparticles

Fe₃O₄ nanoparticles were synthesized following a previously reported procedure with slight modifications. The prepared sample was immersed in 37% HCl at a ratio of 1:2 (w/v) and stirred at 70 °C for 30 minutes. The resulting solution was filtered, and the filtrate was precipitated by the dropwise addition of 20% ammonium hydroxide (NH₄OH) under continuous stirring at 70 °C. The precipitate was then filtered and washed with demineralized water (DM water) until the pH reached

6.5. Finally, the obtained solid was dried at 120 °C for 8 hours (Gano et al., 2024).

2.3 Synthesis of ZIF-67 and ZIF-67@Fe₃O₄ (ZIFO)

ZIF-67 was synthesized by dissolving 48 mmol of 2-methylimidazole and 12 mmol of Co(NO₃)₂·6H₂O in 150 mL of methanol. The two solutions were combined and stirred using a shaker at 150 rpm for 30 minutes, followed by aging at room temperature for 24 hours. The resulting precipitate was collected by centrifugation, washed three times with methanol, and dried at 100 °C for 24 hours (Lei et al., 2023). The ZIF-67@Fe₃O₄ (ZIFO) composite was synthesized using the same procedure as ZIF-67. The primary difference was the incorporation of 0.08 g of Fe₃O₄ into the 2-methylimidazole solution prior to mixing.

2.4 Characterization

The crystallographic structures of ZIF-67 and the synthesized ZIFO composites were analyzed by X-ray diffraction (XRD, Bruker D6-Phaser) using Cu K α radiation (λ = 1.545 Å), operated at 40 kV and 15 mA. Diffraction patterns were recorded over a 2θ range of 5–80° at a scanning rate of 2° min⁻¹ with a step size of 0.04°. The surface morphology, particle distribution, and elemental composition of the samples were examined using field-emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FESEM-EDS, HITACHI SU8220) at an accelerating voltage of 2 kV. High-resolution micrographs were obtained at magnifications ranging from 2,000× to 60,000×. The textural properties, including the specific surface area and pore characteristics, were evaluated from N₂ adsorption–desorption isotherms at 77.3 K using a Quantachrome QuadraWin system. Prior to measurement, the samples were degassed under vacuum at 150 °C for 5 h to remove physically adsorbed moisture, residual solvents, and gaseous impurities. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, while the total pore volume was determined from the nitrogen adsorption amount at a relative pressure (P/P_0) of 0.991. Molecular structure and chemical bonding were further investigated by Raman spectroscopy (Bruker Senterra II) using a 785 nm excitation laser with an output power of 10 mW and an aperture of 50 × 1000 μ m. The spectra were collected over the range of 45–3630 cm⁻¹ with a spectral resolution of 4 cm⁻¹. Functional groups were identified by attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR, Bruker Alpha I), with spectra recorded in the range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹ over 64 scans. The surface chemical composition and oxidation states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS, DESKTOP-TFLCH0R) equipped with a monochromatic Al K α radiation source ($h\nu$ = 1491.690 eV). Measurements were performed under ultra-high vacuum conditions ($\sim 10^{-9}$ mbar) with an accelerating voltage of 12 kV and an operating power of 75 W. The optical absorption properties of the samples were analyzed using UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS,

Shimadzu UV-2401-PC). The obtained zeta potential values were used to assess the surface charge characteristics, colloidal stability, and pH-dependent adsorption behavior of the adsorbents toward Pb(II) ions. The concentrations of Pb(II) ions before and after adsorption were determined by atomic absorption spectroscopy (AAS, PerkinElmer Analyst-100) at a wavelength of 217 nm.

2.5 Adsorption Experiment

Batch adsorption experiments were systematically conducted to evaluate the effects of various operational parameters on the Pb(II) removal efficiency. In a typical experiment, 15 mg of adsorbent (ZIF-67 or ZIFO) was dispersed into 15 mL of Pb(II) solution (150 mg L⁻¹) contained in 30 mL glass vials. The suspensions were agitated at 150 rpm using an orbital shaker at ambient temperature until equilibrium was reached.

To optimize adsorption performance, the effects of solution pH (4, 5, 6, 8, and 9), contact time (10, 20, 30, 40, 50, and 60 min), and initial Pb(II) concentration (30, 50, 70, 100, and 150 mg L⁻¹) were investigated. The pH was adjusted using 0.1 M HCl or 0.1 M NaOH solutions. After adsorption, the solid adsorbent was separated, and the residual Pb(II) concentration was measured using AAS at 217 nm. The removal efficiency (Re, %) and equilibrium adsorption capacity (q_t, mg g⁻¹) were calculated using Equations (1) and (2), respectively (Tu et al., 2018):

$$\text{Removal Efficiency (Re) (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

Where C_o and C_t (mg L⁻¹) represent the initial and time-dependent Pb(II) concentrations, respectively; V (L) is the solution volume; and m (g) is the mass of the adsorbent. To further elucidate the adsorption mechanism, kinetic studies were performed by adding 15 mg of adsorbent to 15 mL of 150 mg L⁻¹ Pb(II) solution. After agitation at ambient temperature for predetermined time intervals (10, 20, 30, 40, 50, and 60 min), the adsorbent was separated, and the remaining Pb(II) concentration was determined using AAS. The kinetic data were analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO) models, expressed in Equations (3) and (4) (Tu et al., 2018):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad (4)$$

where q_e and q_t (mg g⁻¹) denote the adsorption capacities at equilibrium and at time t (min), respectively; k_1 (min⁻¹)

and k_2 (g mg⁻¹ · min⁻¹) are the rate constants of the PFO and PSO models. Adsorption isotherms were evaluated by varying the initial Pb(II) concentration (30–150 mg L⁻¹) at a fixed ZIFO dosage of 1 g L⁻¹ for 30 minutes. The equilibrium data were fitted to the Langmuir (Equation 5) and the Freundlich (Equation 6) isotherm models (Huang et al., 2025):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

where C_e (mg L⁻¹) is the equilibrium concentration of Pb(II); q_m (mg g⁻¹) represents the maximum monolayer adsorption capacity; K_L (L mg⁻¹) is the Langmuir constant related to binding affinity; and K_F [(mg g⁻¹) · (L mg⁻¹)^{1/n}] and n are the Freundlich constants describing adsorption capacity and intensity, respectively. The equilibrium thermodynamic parameters, including the Gibbs free energy change (ΔG^0 , kJ mol⁻¹), the enthalpy change (ΔH^0 , kJ mol⁻¹) and the entropy change (ΔS^0 , J (mol K)⁻¹) were calculated through Equations (7) – (9) on the basis of experimental data to investigate the thermodynamic behavior of Pb(II) adsorption onto as-prepared ZIF-67@Fe₃O₄. The thermodynamic properties were studied under the conditions of 150 mg L⁻¹, and at different temperatures (298 K, 308 K, 313 K, 318 K).

$$K_c = \frac{q_e}{c_e} \quad (7)$$

$$\Delta G^0 = -RT \ln K_c \quad (8)$$

$$\ln K_c = -\frac{\Delta H^0}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{R} \quad (9)$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), and K_c is the equilibrium constant.

3. RESULT AND DISCUSSION

3.1 Structural and Chemical Characterization

The crystal structures of Fe₃O₄, ZIF-67, and the ZIF-67@Fe₃O₄ (ZIFO) composite were characterized using X-ray diffraction (XRD), as shown in Figure 1a. The diffraction pattern of the synthesized Fe₃O₄ (1a, green line) exhibits characteristic peaks at $2\theta = 30.2^\circ$ (220), 35.6° (311), 43.2° (400), 53.8° (422), 57.3° (511), and 62.9° (440), corresponding to the cubic magnetite phase (JCPDS No. 065-0731). These results confirm the successful formation of Fe₃O₄ with good crystallinity. In the XRD pattern of the ZIF-67@Fe₃O₄ (ZIFO) composite, the characteristic peaks of Fe₃O₄ remain clearly observable

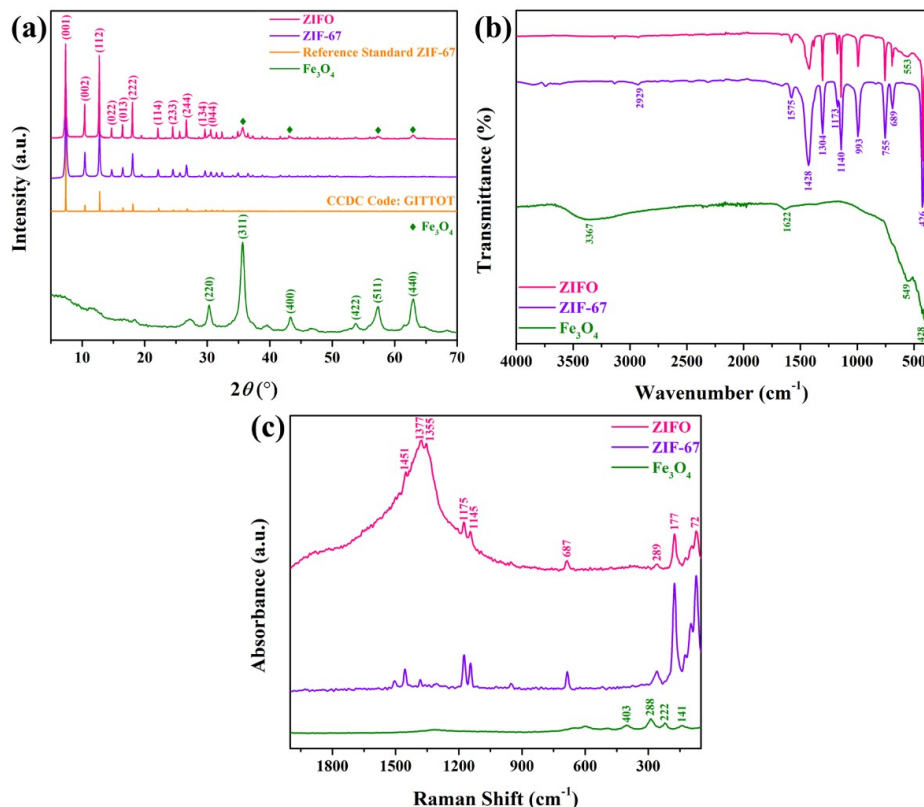


Figure 1. (a) XRD, (b) FTIR, (c) Raman Spectra of Fe_3O_4 , ZIF-67, and ZIF-67@ Fe_3O_4 (ZIFO)

without significant shifts in peak positions, indicating that the magnetite crystal structure was preserved during composite formation. In addition, the composite diffraction pattern (1a, pink line) displays the typical reflections of ZIF-67 at $2\theta = 7.3^\circ, 10.3^\circ, 12.7^\circ, 14.7^\circ, 16.4^\circ, 18.0^\circ, 22.1^\circ, 24.5^\circ, 26.6^\circ, 29.6^\circ, 30.5^\circ,$ and 35.6° , which are indexed to the (001), (002), (112), (022), (013), (222), (114), (233), (244), (134), (044), and (311) crystal planes, respectively. All diffraction peaks are well-defined and consistent with previously reported crystal patterns of ZIF-67 (Jiang et al., 2023; Maryanti et al., 2025; Song et al., 2022; Lei et al., 2023), confirming the successful formation of a highly crystalline ZIF-67 framework. No impurity phases or significant peak shifts were detected, suggesting that the incorporation of Fe_3O_4 nanoparticles did not disrupt the crystalline framework of ZIF-67. Instead, the composite retained its crystallinity and structural stability. These findings indicate that Fe_3O_4 nanoparticles were successfully dispersed within the ZIF-67 matrix without compromising its structural order.

The crystallite size average can be calculated using the Equation Debye-Scherrer.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (10)$$

where D (nm)-average crystalline sizes, k-wave constant=0.9,

λ =wavelength of the X-ray radiations ($\lambda=0.154$ nm) ($\text{CuK}\alpha$), θ -Bragg diffractions angles as well as β -full width at half maximum (FWHM) of the respective diffractions peak.

The crystallite size parameters of ZIF-67, Fe_3O_4 , and the ZIF-67/ Fe_3O_4 (ZIFO) composite are summarized in Table 2. The average crystallite sizes obtained from the most intense diffraction peaks were 37.06 nm for ZIF-67 and 9.05 nm for Fe_3O_4 , consistent with previously reported values for similar MOF and magnetite nanostructures (Cravillon et al., 2011; Zargartalebi and Rafiee, 2026). Crystallite size estimation was performed using the Debye-Scherrer equation based on the most intense reflections of ZIF-67 ((001), (002), (112)) and Fe_3O_4 ((220), (311), (400), (511)).

For the ZIF-67/ Fe_3O_4 (ZIFO) composite, the average crystallite size increased to 46.37 nm (Table 2). This increase suggests that Fe_3O_4 nanoparticles act as heterogeneous nucleation centers during in situ crystallization, facilitating the growth of larger ZIF-67 crystalline domains. Similar nucleation-assisted crystal growth behavior in MOF-nanoparticle hybrid systems has been previously reported (Shearer et al., 2016). In addition, the ZIFO composite exhibits higher diffraction intensities and reduced FWHM values compared to the individual components, indicating improved crystallinity and enhanced structural ordering of the heterostructure.

The functional groups and chemical coordination of Fe_3O_4 , ZIF-67, and the ZIF-67@ Fe_3O_4 (ZIFO) composite were ana-

Table 1. Comparative Analysis of Synthesis Strategies, Structural Characteristics, and Morphologies of Representative ZIF-67- and Fe₃O₄-Based Composites.

Material	Synthesis Method	XRD	Morphology (SEM/FESEM)	Ref
ZIF-67	Hydrothermal	ZIF-67 peaks confirmed	Polyhedral structure	(Li et al., 2022)
ZIF-67	Solution synthesis	ZIF-67 sharp peaks	Rhombic dodecahedral crystals	(Li et al., 2015)
ZIF-67@GA	Sonication-assisted magnetic stirring	Not reported	Chamfered cubes	(Raj et al., 2026)
ZIF-67	Solvothermal	ZIF-67 sharp peaks	Rhombic dodecahedral crystals	(Mostafazadeh et al., 2018)
Fe ₃ O ₄ /ZIF-67@AmCs beads	Ex-situ growth	Not reported	Core-double shell	(Omer et al., 2021)
ZIF-67@Cs	In-situ growth	ZIF-67 sharp peaks dominated	Porous and ZIF-67 is evenly distributed coated by CS	(Fu et al., 2022)
ZIF-67	Solution synthesis	ZIF-67 sharp peaks	Rhombic dodecahedral crystals	(Xie et al., 2023)
ZIF-67	Solvothermal	Similar diffraction pattern to single-crystal ZIF-67	Wafer-like morphology	(Huang et al., 2018)
Cu-MOFs/Fe ₃ O ₄	Hydrothermal	Not reported	Spherical-flower like	(Shi et al., 2018)
Fe ₃ O ₄ -FeMoS ₄	Hydrothermal	Hydrotalcite characteristic pattern	Nano-metric spherical	(Behbahani et al., 2021)
Fe ₃ O ₄ @C	Co-precipitation	Cubic	Rough porous surface	(Kakavandi et al., 2015)
Fe ₃ O ₄	Co-precipitation	Cubic spinel	Spherical	(Li et al., 2022)
ZIF-67@Fe ₃ O ₄	Solvothermal	ZIF-67 sharp peaks	Rhombic dodecahedral	This work

Table 2. The Average Crystalline Sizes of ZIF-67, Fe₃O₄ and ZIFO Composite

Material	2θ (°)	FWHM (°)	Crystallite Size (nm)	Average Crystallite Size (nm)
ZIF-67	7.394	0.26686	29.832	37.06
	10.421	0.21517	37.074	
	12.760	0.20447	39.095	
	18.058	0.1904	42.248	
Fe ₃ O ₄	30.280	0.73264	10.466	9.05
	35.624	0.79313	9.536	
	43.232	0.66844	11.045	
	57.350	1.02957	6.836	
ZIFO	7.449	0.20468	38.895	46.37
	10.499	0.18594	42.905	
	12.847	0.16457	48.578	
	18.15788	0.14594	55.126	

lyzed using Fourier-transform infrared (FTIR) spectroscopy, as presented in Figure 1b. The FTIR spectrum of Fe₃O₄ (Figure 1b, green line) exhibits a prominent absorption band at 549 cm⁻¹, characteristic of the Fe–O stretching vibration in the magnetite lattice. Additionally, the broad bands observed at 3367 cm⁻¹ and 1622 cm⁻¹ are attributed to the stretching and bending vibrations of hydroxyl (–OH) groups originating from physically adsorbed water molecules. In the ZIF-67 spectrum (1b, purple line), the successful coordination between Co²⁺ ions and the nitrogen atoms of the 2-methylimidazole

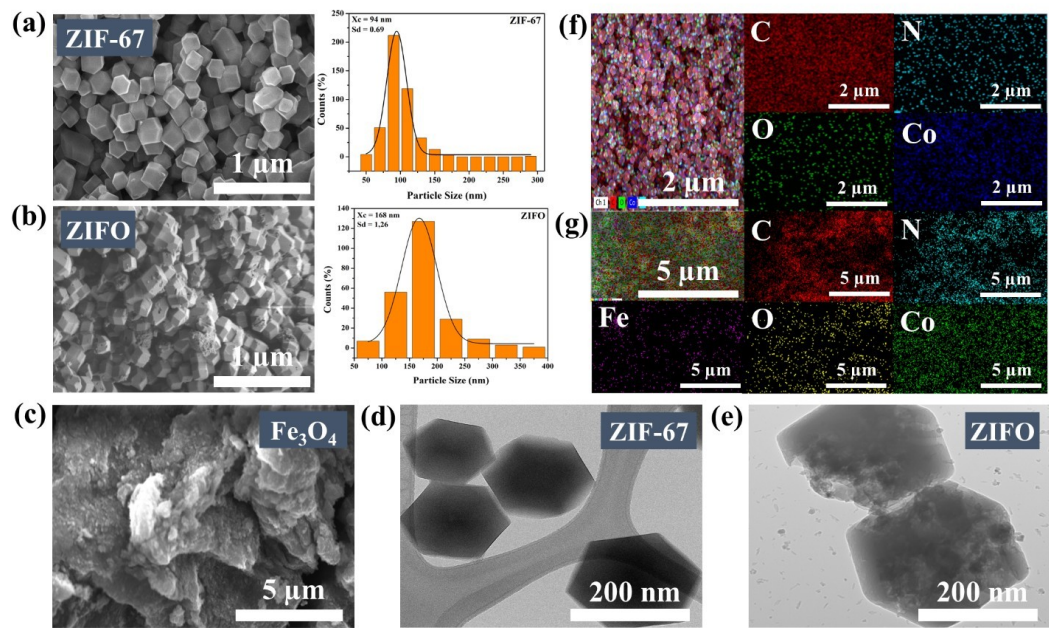


Figure 2. (a) FESEM ZIF-67, (b) FESEM ZIF-67@Fe₃O₄ (ZIFO), (c) SEM Fe₃O₄, (d) HR-TEM ZIF-67, (e) HR-TEM ZIF-67@Fe₃O₄, (f) EDS Elemental Mapping of ZIF-67, and (g) EDS Elemental Mapping of ZIF-67@Fe₃O₄

Table 3. Elemental Composition of ZIF-67 and ZIFO Determined by EDS Analysis

Element (%w/t)	ZIF-67		ZIFO	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	67.73	75.73	92.93	95.75
N	18.71	17.94	3.22	2.84
O	5.31	4.44	1.05	0.81
Fe	-	-	0.82	0.18
Co	8.24	1.88	1.98	0.42

ligand is confirmed by the Co–N stretching vibration at 426 cm⁻¹, consistent with previously reported values around 419 cm⁻¹ (Maryanti et al., 2025). The FTIR spectrum of ZIF-67 shows characteristic absorption bands corresponding to the functional groups of the organic ligand. The band at 1575 cm⁻¹ is assigned to the C=N stretching vibration, while the peak at 2929 cm⁻¹ corresponds to the sp³ C–H stretching vibration of the methyl group, in agreement with previous reports (Jiang et al., 2023; Maryanti et al., 2025; Sadiq et al., 2023; Qian et al., 2012). After incorporation of Fe₃O₄, the FTIR spectrum of the ZIF-67/Fe₃O₄ composite (ZIFO) exhibits the characteristic vibrational bands of both ZIF-67 and Fe₃O₄, confirming the successful formation of the composite structure. The retention of the C=N stretching band at 1575 cm⁻¹ and the out-of-plane bending vibration at 775 cm⁻¹ indicates that the structural integrity of the ZIF-67 framework was maintained after Fe₃O₄ incorporation.

A detailed comparison of the spectra reveals slight shifts

in the characteristic metal–ligand vibrational bands, indicating interfacial interactions between the Fe₃O₄ nanoparticles and the ZIF-67 framework. Specifically, the Fe–O stretching vibration shifted from 549 cm⁻¹ to 553 cm⁻¹, while the Co–N vibration shifted from 426 cm⁻¹ to 422 cm⁻¹. These changes suggest modification of the local coordination environment and electron distribution at the Fe₃O₄/ZIF-67 interface. Furthermore, the presence of the Fe–O vibration band confirms the successful incorporation of Fe₃O₄ nanoparticles into the ZIF-67 matrix, supporting the formation of a ZIFO heterostructure rather than a simple physical mixture.

The Raman spectrum of the ZIF-67@Fe₃O₄ (ZIFO) composite exhibits several characteristic bands, as shown in Figure 1c. The observed peaks at 72, 177, 289, 687, 1145, 1175, 1355, 1377, and 1451 cm⁻¹ are consistent with previous reports (Maryanti et al., 2025; Xue et al., 2022), confirming the presence of vibrational modes characteristic of the composite structure. The band at 1145 cm⁻¹ can be assigned to vibrational

modes of the imidazolate linker within the ZIF-67 framework, particularly C–N stretching and ring-related vibrations. Its presence indicates that the organic ligand structure of ZIF-67 was retained after Fe_3O_4 incorporation, supporting the successful formation of the ZIF-67@ Fe_3O_4 composite. The presence of this band indicates local structural defects within the material, which may influence the electronic properties and surface activity of the composite.

3.2 Morphology and Composition

The surface morphology and elemental distribution of Fe_3O_4 , ZIF-67, and the ZIF-67@ Fe_3O_4 (ZIFO) composite were characterized using SEM, FESEM, and HR-TEM (Figure 2a–g). FESEM images revealed that pristine ZIF-67 exhibits a uniform rhombic dodecahedral morphology with a smooth surface and an average particle size of 96 nm (Figure 2a). In contrast, Fe_3O_4 nanoparticles display a rough texture with a strong tendency toward agglomeration (Figure 2c). For the ZIFO composite (Figure 2b), the characteristic dodecahedral framework of ZIF-67 remains preserved; however, its surface becomes irregular due to the deposition of Fe_3O_4 nanoparticles at the crystal interface. The increase in composite particle size to 168 nm correlates with the aggregation of Fe_3O_4 nuclei formed during the early nucleation stage, consistent with previous findings (Chen et al., 2021). HR-TEM analysis (Figure 2e) further confirms that Fe_3O_4 nanoparticles are uniformly distributed on the surface of ZIF-67 crystals. Elemental mapping in Figure 2g validates the successful synthesis through the detection of C, N, O, and Co elements constituting the ZIF-67 framework, along with Fe representing the magnetite phase. The elemental composition and distribution of the synthesized materials were analyzed using Energy-Dispersive X-ray Spectroscopy (EDS). As summarized in Table 3, pristine ZIF-67 mainly consists of C (67.73 wt%, 75.73 at%), N (18.71 wt%, 17.94 at%), and Co (8.24 wt%, 1.88 at%), which correspond to the major components of the cobalt-based zeolitic imidazolate framework. After incorporation of Fe_3O_4 , the ZIFO composite exhibited the presence of Fe (0.82 wt%, 0.18 at%), confirming the successful introduction of the magnetic iron oxide phase. In addition, the Co content decreased to 1.98 wt% (0.42 at%) after composite formation, accompanied by changes in the relative C and N contents, suggesting the contribution of Fe_3O_4 incorporation to the final composite composition.

The EDS elemental mapping further demonstrates the uniform distribution of C, N, Co, Fe, and O throughout the composite structure. Together with the structural characterization results, these elemental analyses confirm the successful fabrication of the ZIFO composite and provide additional support for its application as a magnetic adsorbent for Pb(II) removal.

3.3 Optical-Vibration Properties and Surface Area

Figure 3a and 3b present the optical properties of ZIF-67 and the ZIF-67@ Fe_3O_4 composite analyzed using UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). The synthesized materials exhibit absorption in the visible light region. ZIF-67

shows an absorption edge at 532 nm (2.3 eV), indicating its remarkable optical properties associated with its porous structure and unique surface characteristics. Meanwhile, the ZIF-67@ Fe_3O_4 composite exhibits absorption at 643 nm (1.93 eV). The observed decrease in the optical band gap of ZIF-67 after integration with Fe_3O_4 is attributed to the formation of a heterostructure composite, as Fe_3O_4 nanoparticles can introduce additional electronic states within the band structure. The incorporation of Fe_3O_4 facilitates electronic interactions and charge transfer at the interface between the Fe_3O_4 and ZIF-67 phases, effectively narrowing the energy gap between the valence band and conduction band (Mahmoud et al., 2024).

The textural properties, including porosity and surface area of the synthesized materials, were analyzed using N_2 adsorption-desorption isotherms based on the BET method (Figure 3c). The synthesized ZIF-67 exhibits a surface area of $990.239 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.039 \text{ cm}^3 \text{ g}^{-1}$, whereas the surface area of the ZIF-67@ Fe_3O_4 composite decreases to $462.571 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.125 \text{ cm}^3 \text{ g}^{-1}$. Detailed porosity parameters of ZIF-67 and the ZIF-67@ Fe_3O_4 composite are presented in Table 4. Based on Figure 3c, the ZIF-67 isotherm demonstrates Type I microstructure characteristics, typical of microporous materials, consistent with previous studies (Maryanti et al., 2025). In contrast, the ZIF-67@ Fe_3O_4 composite exhibits a Type IV microstructure according to IUPAC classification, with an H3 hysteresis loop in the relative pressure range ($P/P_0 > 0.3$). This indicates that the pore structure is no longer dominated by the micropores of ZIF-67 but instead forms a hierarchical micro-mesoporous structure. This structural transformation is attributed to partial pore blockage and the formation of interparticle mesopores at the ZIF-67@ Fe_3O_4 interface due to the integration of Fe_3O_4 particles into the ZIF framework, in agreement with previous reports (Zhao et al., 2019).

Although the incorporation of Fe_3O_4 into the ZIF-67 framework resulted in a lower specific surface area compared with pristine ZIF-67, the ZIF-67@ Fe_3O_4 composite exhibited enhanced Pb(II) adsorption performance. This reduction in surface area can be attributed to the mass dilution effect of the Fe_3O_4 phase and partial blocking of microporous channels during composite formation (Zhang et al., 2022). However, the increased adsorption capacity indicates that Pb(II) removal is not solely dependent on the available surface area. Instead, the adsorption process is strongly influenced by surface chemistry and the generation of additional active adsorption sites.

The incorporation of Fe_3O_4 introduces Fe–O-containing surface groups and hydroxyl functionalities that can interact with Pb(II) ions through surface complexation. In addition, the ZIF-67 framework contributes nitrogen-containing imidazolate groups and exposed Co-based coordination sites, which provide additional interaction sites for Pb(II) adsorption. The interfacial interaction between Fe_3O_4 and ZIF-67 may further modify the surface properties of the composite, improving the accessibility and affinity of adsorption sites (Wang et al., 2022). Similar observations have been reported for magnetic

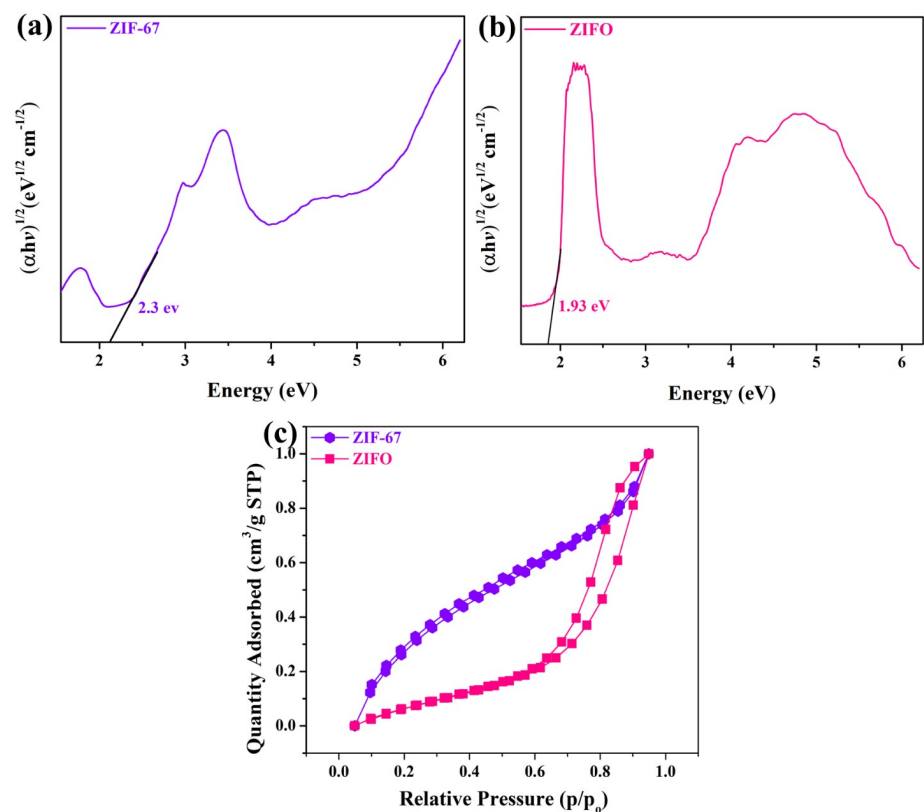


Figure 3. UV-Vis DRS Spectra of (a) ZIF-67, (b) ZIF-67@Fe₃O₄ (ZIFO), and (c) N₂ Adsorption-Desorption Isotherms

Table 4. The Surface Area and Pore Volume of ZIF-67 and ZIF-67@Fe₃O₄

Materials	S _{BET} (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
ZIF-67	990.239	0.039
ZIF-67@Fe ₃ O ₄	462.571	0.125

MOF-based adsorbents, where enhanced adsorption capacity is often associated with increased chemical affinity and active site availability rather than surface area alone (Wang et al., 2025). Therefore, the synergistic contribution of ZIF-67 and Fe₃O₄ compensates for the reduction in BET surface area by providing more favorable adsorption sites and stronger interactions with Pb(II) ions.

The surface chemical composition and oxidation states of the synthesized ZIFO composite were investigated by X-ray photoelectron spectroscopy (XPS), as shown in Figure 4(a-c). The survey spectrum (Figure 4a) reveals the characteristic peaks corresponding to C 1s, N 1s, O 1s, Fe 2p, and Co 2p, confirming the presence of both the ZIF-67 framework and Fe₃O₄ phase in the composite. The coexistence of Co- and Fe-containing species indicates the successful formation of the ZIF-67@Fe₃O₄ heterostructure (Eltaweil et al., 2023).

The high-resolution Fe 2p spectrum of ZIFO (Figure 4c) exhibits the characteristic Fe 2p_{3/2} and Fe 2p_{1/2} peaks located at approximately 710–711 eV and 723–724 eV, respectively. The

deconvolution of the Fe 2p spectrum reveals the coexistence of Fe(II) and Fe(III) species, confirming the mixed-valence nature of the Fe₃O₄ phase. The presence of these characteristic oxidation states demonstrates that the Fe₃O₄ component was successfully incorporated into the ZIF-67 structure while maintaining its chemical properties (Atrei et al., 2022; Delgado-Marin et al., 2024).

The high-resolution Co 2p spectrum (Figure 4b) displays the Co 2p_{3/2} and Co 2p_{1/2} peaks at approximately 780 and 796 eV, respectively. The fitted peaks indicate the presence of Co(II) and Co(III) species, which are associated with the cobalt coordination environment of the ZIF-67 framework (Eltaweil et al., 2023; Delgado-Marin et al., 2024). The preservation of Co-related chemical states after Fe₃O₄ incorporation suggests that the structural integrity of ZIF-67 was maintained during composite formation.

The simultaneous presence of mixed-valence Fe species and Co-based active centers, together with N- and O-containing functional groups from the ZIF-67 framework, provides abun-

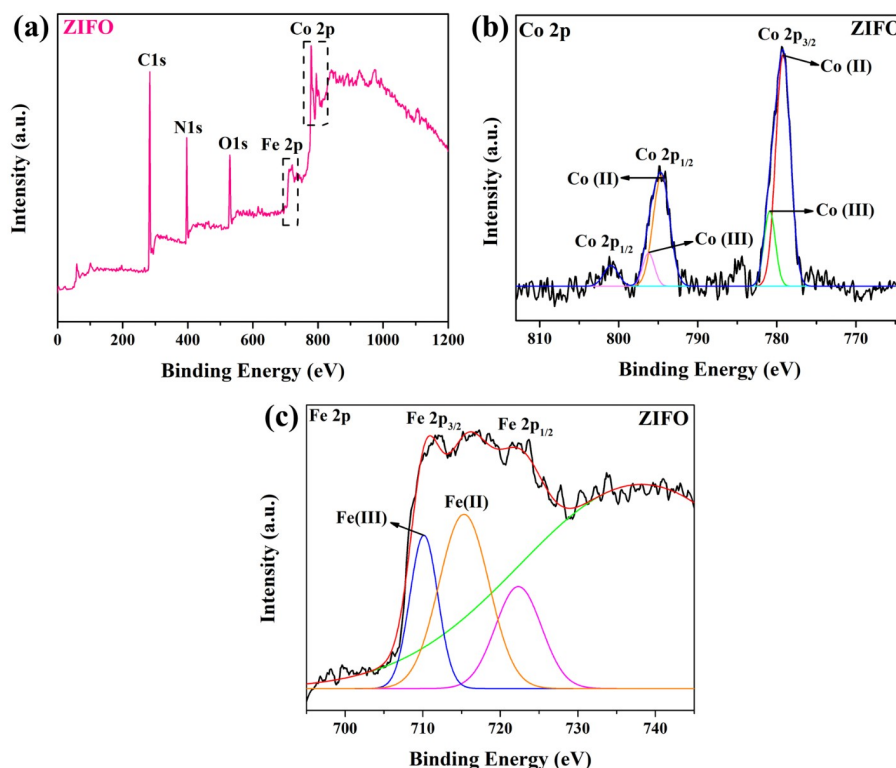


Figure 4. XPS Spectra of ZIF-67@Fe₃O₄ (ZIFO): (a) Survey Spectrum Showing C, N, O, Fe, and Co, (b) High-Resolution Co 2p Spectrum Showing Co(II)/Co(III) Species, and (c) High-Resolution Fe 2p Spectrum Showing Fe(II)/Fe(III) Species, Confirming the Formation of the ZIFO Composite

dant surface sites that may contribute to Pb(II) adsorption through surface complexation and electrostatic interactions. Therefore, the XPS results confirm the successful construction of the ZIF-67@Fe₃O₄ composite and support the availability of chemically active surface sites responsible for the enhanced adsorption performance.

3.4 Adsorption Performance

3.4.1 Effect of pH

As shown in Figure 5, the zeta potential analysis was further conducted to experimentally verify the surface charge characteristics and clarify the pH-dependent adsorption behavior of the synthesized adsorbents. Zeta potential measurements revealed values of +31.7 mV for pristine ZIF-67 and +63.0 mV for ZIF-67@Fe₃O₄(ZIFO), respectively. The higher positive surface charge of ZIFO indicates that Fe₃O₄ incorporation significantly modified the surface electrochemical properties of the ZIF-67 framework. This change can be associated with the introduction of Fe–O-containing surface groups and hydroxyl functionalities from Fe₃O₄, which generate additional active interfaces for adsorption. Similar enhancements in surface charge modulation, stability, and adsorption performance of magnetic MOF composites have been widely reported in recent Fe₃O₄@MOF hybrid systems (Wang et al., 2023; Eltaweil

et al., 2023; Jiang et al., 2021).

The positive zeta potential values indicate that protonation of surface functional groups occurs in aqueous environments, particularly involving nitrogen-containing imidazole ligands and exposed metal coordination sites. Under acidic conditions, excessive protonation increases positive surface charge density, resulting in electrostatic repulsion toward Pb²⁺ ions and competition with H⁺ ions for active sites. This pH-dependent surface charge behavior is consistent with previous reports on ZIF-based materials and magnetic MOF hybrids, where surface protonation strongly regulates heavy metal uptake (Eltaweil et al., 2023; García et al., 2021).

As the pH increases toward neutral conditions, gradual deprotonation reduces electrostatic repulsion and promotes Pb²⁺ interaction with adsorption sites. The enhanced adsorption efficiency of ZIFO at pH 5–8 can therefore be attributed to electrostatic attraction, surface complexation, and coordination bonding between Pb²⁺ ions and both imidazolate nitrogen groups and Fe–OH surface species. Recent studies on Fe₃O₄@MOF composites have shown that Fe–OH groups play a key role in binding heavy metal ions through inner-sphere complexation, significantly improving adsorption capacity and kinetics (Wang et al., 2023; Eltaweil et al., 2023; Jiang et al.,

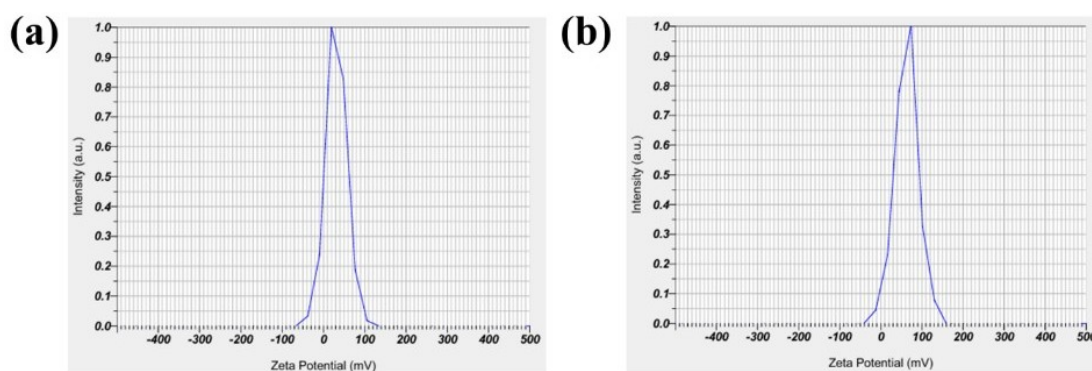


Figure 5. Zeta Potential of (a) ZIF-67 and (b) ZIF-67@Fe₃O₄ (ZIFO) Measured in Aqueous Suspension

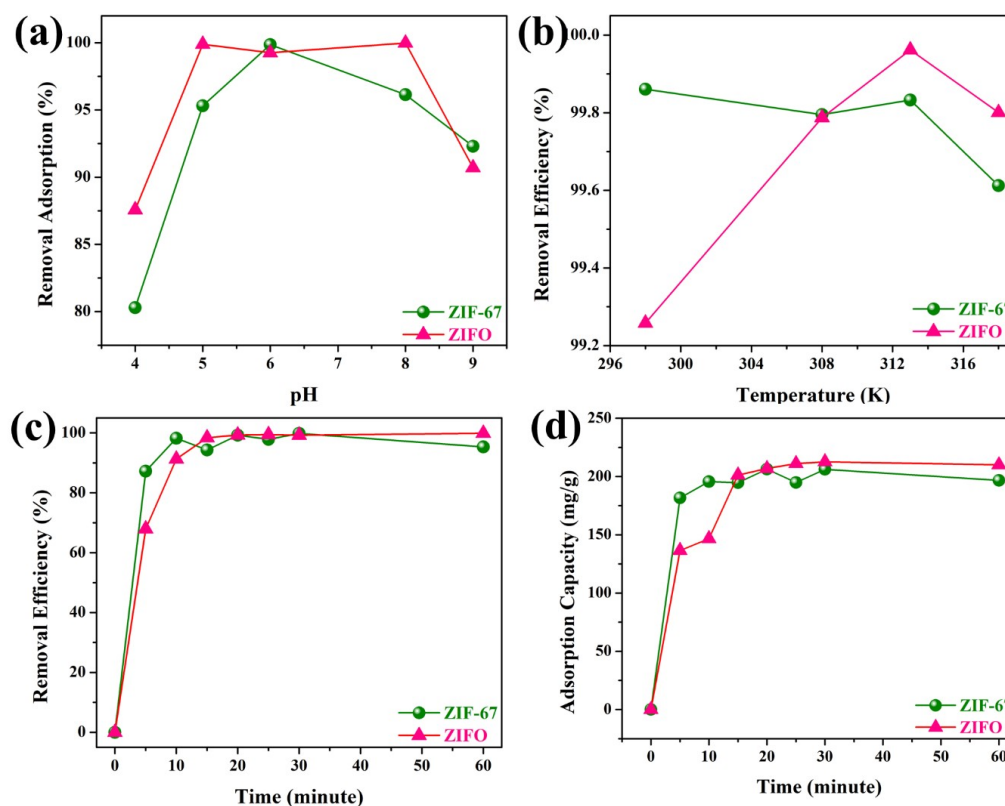


Figure 6. Influence of (a) pH, (b) Temperature, (c) Removal Efficiency and (d) Adsorption Capacity of ZIF-67 and ZIF-67@Fe₃O₄ for Pb(II)

2021).

Furthermore, the higher zeta potential magnitude of ZIFO compared with pristine ZIF-67 suggests improved colloidal stability and a more chemically active adsorption interface. This finding supports the proposed mechanism where superior Pb(II) removal is governed not only by surface area but also by synergistic effects between modified surface charge, accessible coordination sites, and interfacial Fe₃O₄-ZIF-67 interactions.

The solution pH significantly affects both the surface properties of the adsorbent and the speciation of Pb(II) in aqueous

solution. As a hydrolyzable heavy metal, Pb(II) exhibits pH-dependent chemical forms, where Pb²⁺ is dominant under acidic conditions, while hydrolyzed species such as Pb(OH)⁺ and Pb(OH)₂ may form at higher pH values (Jiang et al., 2023). Therefore, an initial pH range of 4–9 was selected to investigate the Pb(II) adsorption behavior of ZIF-67@Fe₃O₄ under different conditions.

The adsorption behavior of Pb(II) is closely related to the surface charge characteristics of the adsorbent. Zeta potential analysis confirmed that ZIF-67 and ZIFO possessed positive

surface charges of +31.7 and +63.0 mV, respectively. The increased surface charge of ZIFO indicates that Fe_3O_4 incorporation modified the surface properties of ZIF-67 by introducing Fe–O-containing groups and hydroxyl functionalities, which provide additional active sites for Pb(II) interaction (Du et al., 2017).

At acidic pH (pH 4), excessive protonation of surface functional groups increases positive surface charge density, causing stronger repulsion toward Pb^{2+} ions and competition with H^+ ions for adsorption sites, resulting in lower removal efficiency. Similar pH-dependent behavior has been reported for ZIF-based materials, where protonation of imidazolate ligands affects adsorption site availability (Singh et al., 2024; Sajjadi et al., 2018).

As the pH increased toward near-neutral conditions, reduced surface protonation enhanced the accessibility of adsorption sites. As shown in Figure 6a, ZIFO exhibited stable and near-complete Pb(II) removal (~100%) within pH 5–8, showing a broader effective adsorption range than pristine ZIF-67, which reached maximum removal at pH 6 (~99.8%). This improvement is attributed to the synergistic contribution of the ZIF-67 framework and Fe_3O_4 component, including modified surface chemistry and additional Fe–OH active sites. At pH >8, the slight decrease in Pb(II) removal may be related to the formation of hydrolyzed Pb species, such as $\text{Pb}(\text{OH})_2$, which reduces the availability of Pb^{2+} for adsorption (Al-Hazmi et al., 2023).

Therefore, pH 6 was selected as the optimum condition for subsequent experiments. The high adsorption efficiency at near-neutral pH suggests that Pb(II) uptake is mainly governed by specific interactions, including coordination between Pb^{2+} ions and nitrogen-containing imidazolate groups of ZIF-67 and complexation with Fe–OH groups on Fe_3O_4 surfaces. Similar coordination-based adsorption mechanisms have been reported for ZIF-based and magnetic MOF adsorbents (Zhang et al., 2016; Sajjadi et al., 2018).

3.4.2 Adsorption Kinetics

The adsorption kinetics of Pb(II) onto ZIF-67 and ZIF-67@ Fe_3O_4 (ZIFO) were investigated by evaluating the effect of contact time at room temperature. As shown in Figure 7, Pb(II) uptake increased rapidly at the initial stage due to the high concentration gradient, abundant accessible active sites, and strong external surface availability (Huang et al., 2025). After approximately 30 min, the adsorption rate gradually decreased and approached equilibrium, which can be attributed to the progressive occupation of active sites and the reduction in available adsorption driving force.

To further elucidate the adsorption mechanism, pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were applied. The results (Table 5) indicate that ZIF-67 follows the PSO model more closely, as evidenced by its higher correlation coefficient ($R^2 = 0.99535$) and the close agreement between experimental and calculated equilibrium capacities ($q_e(\text{exp}) = 206.13 \text{ mg g}^{-1}$; $q_e(\text{cal}) = 204.57 \text{ mg g}^{-1}$).

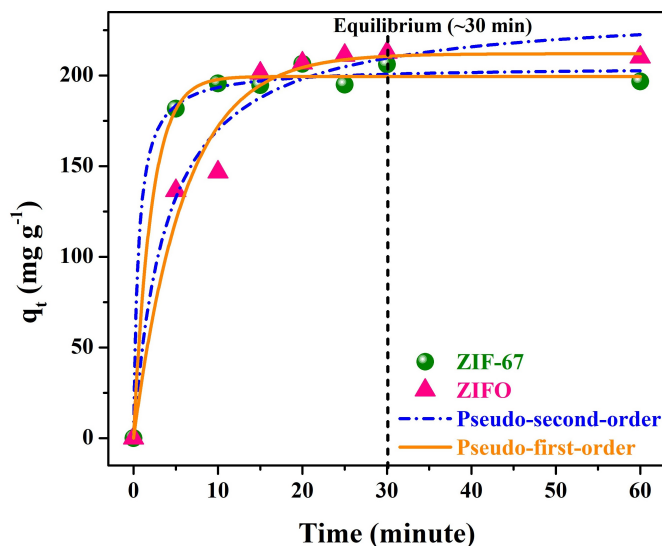


Figure 7. Effect of Contact Time on Pb(II) Adsorption onto ZIF-67 and ZIF-67@ Fe_3O_4 (ZIFO), Fitted with Pseudo-First-Order and Pseudo-Second-Order Kinetic Models at Room Temperature

This suggests that Pb(II) adsorption on ZIF-67 is primarily governed by chemisorption involving valence forces and surface complexation.

In contrast, ZIFO exhibits better agreement with the PFO model, with $q_e(\text{cal})$ (212.00 mg g^{-1}) closely matching the experimental value (212.69 mg g^{-1}), slightly higher R^2 than PSO, and a noticeable deviation in PSO-predicted capacity. This implies that after Fe_3O_4 incorporation, the adsorption process is more influenced by physical interactions such as electrostatic attraction between negatively charged surface sites (Fe/Co-based moieties) and Pb(II) ions, as well as diffusion-controlled mass transfer (Al-Hazmi et al., 2023). Therefore, the modification with Fe_3O_4 alters the dominant adsorption mechanism from chemisorption-controlled (ZIF-67) to more diffusion/physical interaction-controlled behavior (ZIFO).

To compare the initial adsorption rates of the synthesized materials, the pseudo-first-order rate constants (K_1) of pristine ZIF-67 and the magnetic ZIFO composite were evaluated. The K_1 value of ZIF-67 was 0.47818 min^{-1} , which was higher than that of ZIFO (0.1665 min^{-1}), indicating faster initial Pb(II) uptake by pristine ZIF-67. The pristine ZIF-67 exhibits an initial kinetic rate constant that is approximately 2.87-fold higher than that of the ZIFO composite. This difference in the kinetic behavior may be attributed to structural and interfacial changes caused by the in-situ incorporation of Fe_3O_4 . Pristine ZIF-67 possesses more exposed surface sites and relatively open pore pathways, allowing Pb(II) ions to diffuse more readily to the adsorption sites and resulting in a faster initial adsorption rate. Conversely, within the ZIFO hybrid network, the successful in-situ growth of Fe_3O_4 nanoparticle

Table 5. Kinetic Parameters for Pb(II) Adsorption Onto ZIF-67 and ZIF-67@Fe₃O₄ (ZIFO)

Adsorbent	q _{e(exp)} (mg g ⁻¹)	Pseudo-First-Order			Pseudo-Second-Order			
		q _{e(cal)} (mg g ⁻¹)	K ₁ (1 min ⁻¹)	R ²	q _{e(cal)} (mg g ⁻¹)	K ₂ (g min) mg ⁻¹	R ²	
ZIF-67	206.13	199.46±2.089	0.47818±0.058	0.99572	204.57±3.358	0.0085±0.003	0.99535	
ZIFO	212.69	212.00±7.172	0.1665±0.024	0.97419	237.08±12.227	0.0010±3.317	0.97297	

Table 6. Thermodynamic Parameters Calculated for Pb(II) Adsorption with ZIF-67 and ZIF-67@Fe₃O₄

Materials	ΔH ⁰ (kJ mol ⁻¹)	ΔS ⁰ (J mol ⁻¹)	ΔG ⁰ (kJ mol ⁻¹)			
			298 K	308 K	313 K	318 K
ZIF-67	+32.579±2157.84	6.041±6.98	-34.19	-34.33	-35.46	-33.77
ZIF-67@Fe ₃ O ₄	-76.793±6904.79	361.051±22.34	-30.12	-34.32	-39.34	-35.64

introduces a degree of spatial hindrance and increases the intra-particle diffusion resistance within the porous channels, which moderately decelerates the solute migration velocity (K1). Crucially, however, this 2.87-fold decrease in the initial rate constant does not compromise the ultimate remediation efficiency. The in-situ layout optimizes the structural integrity, resulting in an overall upgrade of the total equilibrium adsorption capacity (q_e(exp)) increases from 206.13 mg g⁻¹ for ZIF-67 to 212.69 mg g⁻¹ for ZIFO) due to the generation of new synergistic active sites at the Fe₃O₄/MOFs interface. Although ZIFO showed a slightly lower initial adsorption rate, this limitation is balanced by its magnetic responsiveness, which enables rapid and convenient separation after adsorption. This feature improves the practical applicability of the composite for wastewater treatment.

3.4.3 Thermodynamic Study

The effect of temperature on Pb(II) adsorption by ZIF-67 and ZIF-67@Fe₃O₄ was investigated within the range of 298–318 K (Figure 8a). The adsorption capacity of both adsorbents showed moderate variation with increasing temperature, indicating that temperature influences the adsorption equilibrium. As summarized in Table 6, the calculated δG0 values for both ZIF-67 and ZIF-67@Fe₃O₄ were negative at all investigated temperatures, suggesting that Pb(II) adsorption is a spontaneous process. The variation of δG0 with temperature indicates changes in adsorption favorability as the temperature increases.

The δH0 value provides information regarding the heat effect associated with adsorption. The positive δH0 value obtained for ZIF-67 indicates an endothermic adsorption process, where increased temperature slightly favors Pb(II) uptake. In contrast, the negative δH0 value calculated for ZIF-67@Fe₃O₄ suggests an exothermic adsorption process, indicating stronger interactions between Pb(II) ions and the active sites of the composite surface. The different thermodynamic behaviors may be related to the modified surface environment after incorporation

of Fe₃O₄. The positive δS0 value for ZIF-67@Fe₃O₄ suggests increased randomness at the solid–liquid interface during adsorption, which may result from the displacement of interfacial water molecules and rearrangement of adsorbed Pb(II) species. Therefore, the thermodynamic results indicate that Pb(II) adsorption onto both materials is spontaneous, while the Fe₃O₄ incorporation modifies the adsorption environment and influences the adsorption energetics.

3.4.4 Adsorption Isotherms

The relationship between the equilibrium concentration (C_e) and the adsorption capacity (q_e) is presented in Figure 9. The adsorption capacities (q_{max}) of ZIF-67 and ZIF-67@Fe₃O₄ (ZIFO) increased significantly with increasing initial Pb(II) concentrations, reaching 140.16 mg g⁻¹ and 145.94 mg g⁻¹, respectively. This behavior can be attributed to the enhanced mass transfer driving force at higher concentrations, which effectively overcomes the resistance between the aqueous and solid phases (Huang et al., 2025). The experimental data were fitted using the Langmuir and the Freundlich isotherm models (Figure 9b-c, Table 7). The Langmuir model showed the best fit to the experimental data (R² = 0.9887), indicating that Pb(II) adsorption occurred predominantly as monolayer coverage on energetically homogeneous adsorption sites. To further evaluate the feasibility of the adsorption process, the dimensionless separation factor (RL) was calculated using the equation: RL = 1 / (1 + KL C₀), where KL is the Langmuir constant, and C₀ is the initial concentration. The calculated RL values for both adsorbents at all tested concentrations were within the range of 0 < RL < 1, indicating that the adsorption of Pb(II) onto ZIFO is highly favorable. In contrast, the relatively lower correlation of the Freundlich model (R² = 0.9816) suggests that multilayer adsorption on heterogeneous surfaces is not the dominant mechanism in this system.

Although several highly functionalized adsorbents reported in the literature exhibit higher maximum adsorption capacities,

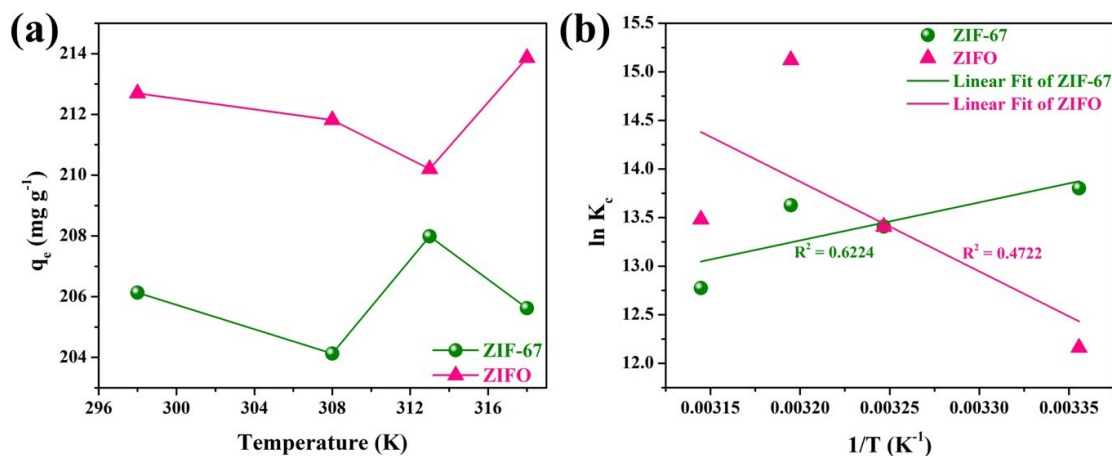


Figure 8. (a) Effect of Adsorption Temperature on the Pb(II) Adsorption Capacity of ZIF-67 and ZIF-67@Fe₃O₄, (b) Van't Hoff Plots of $\ln K_c$ Versus $1/T$ for the Thermodynamic Analysis of Pb(II) Adsorption onto ZIF-67 and ZIF-67@Fe₃O₄

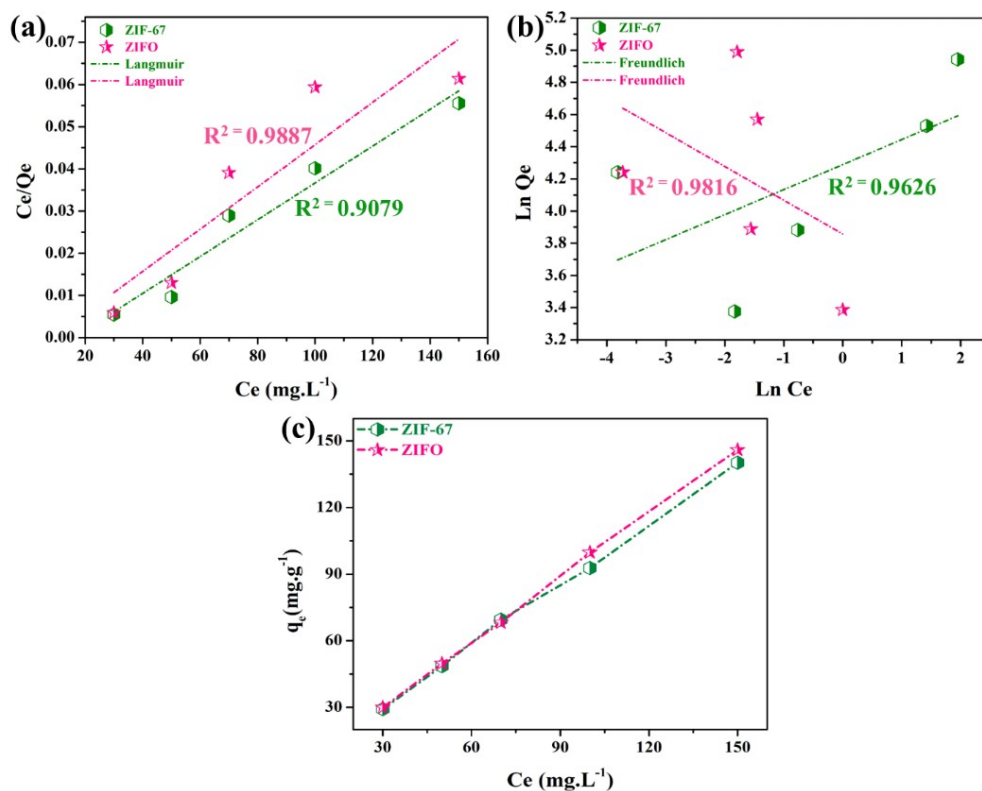


Figure 9. (a) Adsorption Isotherm Fitted by Langmuir Model, (b) Adsorption Isotherm Fitted by Freundlich Model, and (c) Effect of Initial Concentration on the Adsorption Capacity of Pb(II)

ZIFO offers a distinct and practically important advantage by combining rapid adsorption kinetics, facile room-temperature synthesis, preserved ZIF-67 crystallinity, and magnetic separability in a single material platform. This combination is particularly important because many high-capacity adsorbents rely on more complex functionalization strategies or lack sim-

ple post-treatment recovery. Therefore, the present ZIFO composite can be confidently regarded as a highly competitive and practically attractive adsorbent for Pb(II) remediation, especially in applications where easy separation and operational simplicity are essential.

Table 7. Parameters of Isotherm Models for Pb(II) Adsorption by ZIF-67@Fe₃O₄ (ZIFO)

Metal	Adsorbent	Langmuir Model			Freundlich Model		
		q _{max} (mg g ⁻¹)	K _L (L mg ⁻¹)	R _L ²	K _F (mg g ⁻¹)	n (L g ⁻¹)	R _F ²
Pb ²⁺	ZIF-67	137.55	0.3368	0.9079	22.0861	0.4636	0.9626
	ZIFO	158.73	0.5821	0.9887	68.4936	1.1130	0.9816

Table 8. Comparison of ZIF-67@Fe₃O₄ with Other Reported Adsorbents for Heavy Metal Ion Removal

Adsorbent	Metal	Heavy Metal Concentration (mg L ⁻¹)	pH	Adsorbent Dose (g L ⁻¹)	Time (minute)	q _{max} (mg g ⁻¹)	Percentage Adsorption (%)	Ref
ZIF-67	Cr(VI)	80	8	1.67	20	43.1	-	(Li et al., 2022)
ZIF-67	Cr(VI)	15	5	1	20	15.43	88	(Li et al., 2015)
ZIF-67@GA	Pb(II)	10	-	0.5	15	1020	-	(Raj et al., 2026)
ZIF-67	Cr(VI)	107.82	5	0.009	180	26.27	-	(Mostafazadeh et al., 2018)
Fe ₃ O ₄ /ZIF-67@AmCs beads	Cr(VI)	50	2	0.5	-	119.05	77.2	(Omer et al., 2021)
ZIF-67@Cs	Pb(II)	100	7	0.2	240	505.051	-	(Fu et al., 2022)
ZIF-67	Cr(VI)	200	-	1	360	27.7	-	(Xie et al., 2023)
ZIF-67	Pb(II)	200	6	0.5	60	1348.42	~95	(Huang et al., 2018)
Cu-MOFs/Fe ₃ O ₄	Pb(II)	10	-	1	60	219	-	(Shi et al., 2018)
Fe ₃ O ₄ -FeMoS ₄	Pb(II)	40	5	1.5	60	190.75	-	(Behbahani et al., 2021)
Fe ₃ O ₄ @C	Pb(II)	50	6	2	60	-	~90	(Kakavandi et al., 2015)
ZIF-67@Fe ₃ O ₄	Pb(II)	10	6	1	30	212.696	99.25	This work

3.5 The stability of ZIF-67@Fe₃O₄

The practical applicability and economic feasibility of adsorbents for wastewater treatment are largely determined by their regeneration capability and structural stability during repeated adsorption–desorption processes. The cyclic adsorption performance of pristine ZIF-67 and the magnetic ZIFO composite toward Pb(II) ions is presented in Figure 10a. Both materials exhibited excellent initial adsorption efficiencies, achieving Pb(II) removal efficiencies of 99.86% and 99.25%, respectively, during the first cycle. However, after three consecutive regeneration cycles, pristine ZIF-67 showed a noticeable decrease in removal efficiency to 91.50%, indicating a gradual deterioration of adsorption performance under repeated aqueous exposure. The reduced cyclic stability of pristine ZIF-67 can be associated with the inherent susceptibility of the Co-based zeolitic imidazolate framework to hydrolytic degradation. Continuous exposure to water and hydrated metal ions may weaken the Co–N coordination bonds, leading to partial framework distortion, reduced pore accessibility, and decreased availability of adsorption-active sites. This structural instability limits the preservation of nitrogen-containing coordination sites responsible for Pb(II) binding, resulting in progressive adsorption capacity loss during regeneration cycles (Emara et al., 2023). In comparison, the ZIFO composite showed good regeneration stability, maintaining a Pb(II) removal efficiency of 91.34% after three cycles, corresponding to a 7.91% decrease from its initial performance. This recyclability may be associ-

ated with the incorporation of Fe₃O₄, which helps improve the structural integrity of the ZIF-67 framework through interfacial interactions between the Fe₃O₄ phase and the MOF structure. These interactions may reduce framework deformation during repeated adsorption–desorption processes (Chen et al., 2024b). In addition, the magnetic responsiveness of ZIFO enables convenient solid–liquid separation after adsorption, reducing adsorbent loss and improving recovery efficiency. The gradual decline in adsorption efficiency of ZIFO after repeated cycles may result from incomplete regeneration of strongly bound Pb(II) species, particularly those associated with surface complexation at hydroxyl groups (≡Fe–OH) and nitrogen-containing imidazole sites. In addition, minor material loss during repeated washing and magnetic recovery procedures may contribute to the observed decrease in adsorption performance (Wang et al., 2023). Nevertheless, the retention of above 90% Pb(II) removal efficiency demonstrates the excellent recyclability and structural robustness of ZIFO, highlighting its potential as a reusable adsorbent for sustainable heavy-metal remediation (Abdelhameed et al., 2020). The magnetic separability of the synthesized ZIF-67@-Fe₃O₄ nanocomposite was qualitatively evaluated by applying an external NdFeB permanent magnet to the side of the reaction vessel. Upon exposure to the magnetic field, the dispersed dark particles rapidly migrated toward the magnet within a few seconds, resulting in a clear and transparent supernatant. This rapid phase separation indicates that the magnetic responsive-

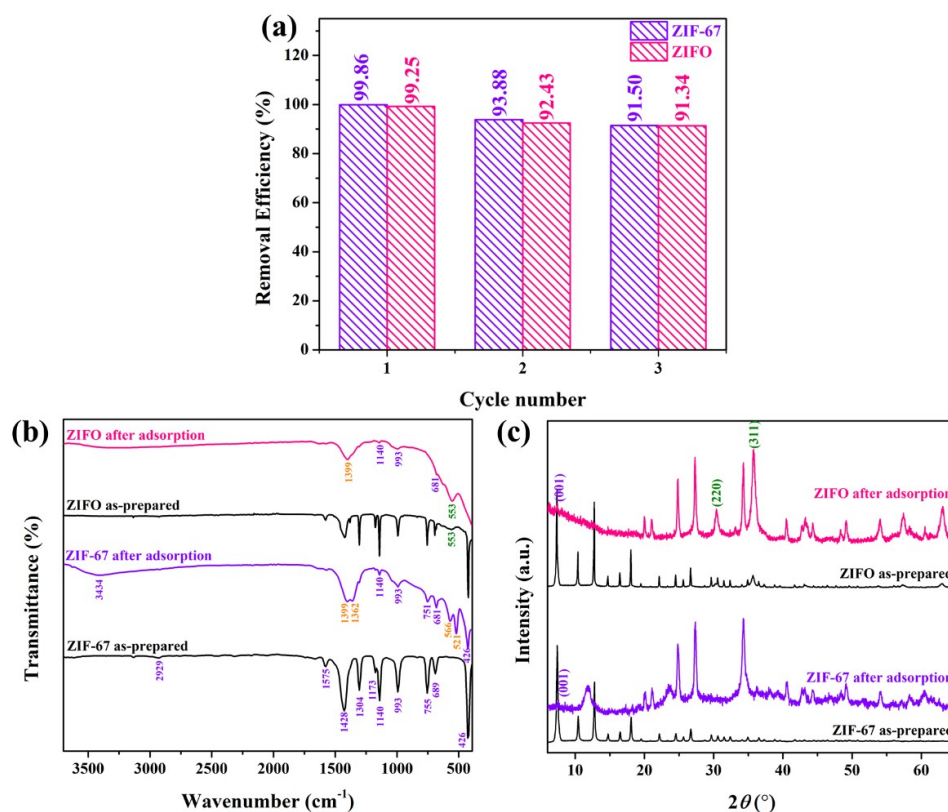


Figure 10. (a) Regeneration and Recycling Performance of ZIF-67 and ZIF-67@Fe₃O₄ for Pb(II) Adsorption, (b) FTIR Spectra, and (c) XRD Patterns of ZIF-67@Fe₃O₄ Before and After Pb(II) Adsorption

ness of the Fe₃O₄ phase was retained after incorporation into the ZIF-67 framework.

Although quantitative magnetic parameters obtained from Vibrating Sample Magnetometer (VSM) analysis, were not measured in this study, the observed magnetic response demonstrates the feasibility of magnet-assisted recovery of the composite. Based on previous reports, Fe₃O₄ nanoparticles generally exhibit high saturation magnetization with low reman

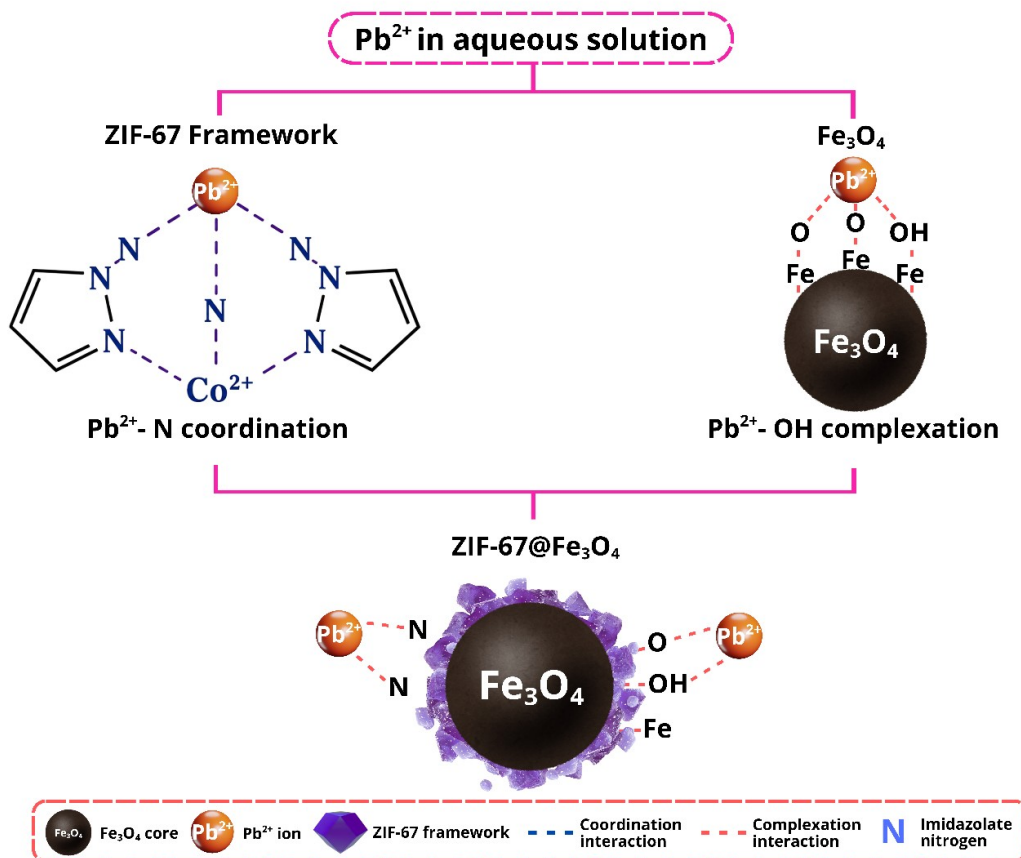


Figure 11. Proposed Adsorption Mechanism of Pb(II) onto ZIF-67@Fe₃O₄ (ZIFO) Composite through Coordination Interactions with Imidazolate Nitrogen Sites, Complexation with Surface Fe–OH Groups, and pH-Dependent Surface Interactions

actions between Pb(II) and surface functional groups without severe framework degradation. Therefore, Pb(II) adsorption on ZIFO is likely governed by coordination interactions involving surface hydroxyl groups and nitrogen donor sites while preserving the composite structure (He et al., 2026). The incorporation of Fe₃O₄ improves the structural stability and recyclability of ZIF-67 while maintaining accessible adsorption sites. The combination of high Pb(II) removal efficiency, magnetic recoverability, and structural durability highlights ZIFO as a promising reusable adsorbent for heavy-metal wastewater treatment.

3.7 Proposed Mechanism for the removal of Pb(II) by ZIF-67@Fe₃O₄

Based on the adsorption proposed mechanism illustrated in Figure 11 and the surface chemical characteristics revealed by XPS analysis, the adsorption of Pb(II) onto ZIFO is suggested to proceed through multiple synergistic pathways involving electrostatic attraction, deprotonation-assisted adsorption, surface complexation, and possible ion-exchange processes. Under appropriate pH conditions, deprotonation of nitrogen-containing

functionalities within the ZIF-67 framework and hydroxyl groups associated with the Fe₃O₄ surface generates negatively charged adsorption sites, which facilitate the initial electrostatic attraction of Pb²⁺ ions toward the adsorbent surface. Concurrently, the desolvation of hydrated Pb²⁺ species reduces the energy barrier for adsorption, enabling closer interaction between Pb²⁺ ions and the active sites distributed throughout the ZIFO heterostructure (Zhou et al., 2020; Chaudhry et al., 2016). Furthermore, the lone pair electrons of nitrogen atoms from the imidazolate linkers and oxygen-containing surface species may coordinate with Pb(II), leading to the formation of stable inner-sphere surface complexes. The proposed mechanism also suggests that partial ion exchange between Pb²⁺ ions and cobalt species within the ZIF-67 framework may contribute to Pb(II) immobilization. Therefore, the superior adsorption performance of ZIFO toward Pb(II) can be attributed to the synergistic effects of electrostatic interactions, deprotonation-assisted adsorption, and surface complexation, with ion exchange potentially serving as an additional adsorption pathway.

4. CONCLUSIONS

In conclusion, a magnetic ZIF-67@Fe₃O₄ (ZIFO) composite was successfully synthesized through a facile methanol-assisted route at ambient temperature and demonstrated excellent performance for Pb(II) removal from aqueous solution. The incorporation of Fe₃O₄ into the ZIF-67 framework not only provided magnetic functionality for easier post-adsorption separation, but also contributed to enhanced adsorption performance. The adsorption behavior was strongly influenced by solution pH, with the optimum removal achieved at pH 6. Kinetic analysis showed that the adsorption process was best described by the pseudo-second-order model ($R^2 = 0.99535$), indicating that chemisorption played a dominant role in Pb(II) uptake. Meanwhile, the equilibrium data were well fitted by the Langmuir isotherm model ($R^2 = 0.9887$), suggesting predominantly monolayer adsorption on homogeneous active sites. Under the optimized conditions, ZIFO exhibited an experimental adsorption capacity of 212.69 mg g⁻¹ with a Pb(II) removal efficiency of 99.86%, while the Langmuir maximum adsorption capacity reached 158.73 mg g⁻¹. Overall, these results confirm that ZIFO is a fast, efficient, and practically attractive adsorbent for Pb(II) remediation. Nevertheless, the structural stability of the composite under acidic conditions remains an important issue for practical implementation. Therefore, future studies should focus on improving the chemical durability and reusability of magnetic MOF-based hybrids, particularly through surface modification, framework stabilization, and validation in real wastewater systems.

5. ACKNOWLEDGEMENT

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REFERENCES

- Abdelhameed, R. M., M. Abu-Elghait, and M. El-Shahat (2020). Hybrid Three MOFs Composites (ZIF-67@ZIF-8@MIL-125-NH₂): Enhancement the Biological and Visible-Light Photocatalytic Activity. *Journal of Environmental Chemical Engineering*, **8**(5); 104107
- Akinawo, S. O., P. O. Ayadi, and M. Temitope (2023). Chemical Coagulation and Biological Techniques for Wastewater Treatment. *Ovidius University Annals of Chemistry*, **34**(1); 14-21
- Al-Hajji, L. A., A. Al-Anazi, A. A. Ismail, A. M. El-Toni, A. Khan, and M. Shkir (2024). A p-n Heterojunction PdO/CeO₂ Photocatalysts with Enhanced Photocatalytic Ability for Reduction of Hg(II) Ions from Aqueous Solution. *Ceramics International*, **50**(22); 45650-45657
- Al-Hazmi, G. H., A. M. A. Adam, M. G. El-Desouky, A. A. El Bindary, A. M. Alsuhaibani, and M. S. Refat (2023). Efficient Adsorption of Rhodamine B Using a Composite of Fe₃O₄@ZIF-8: Synthesis, Characterization, Modeling Analysis, Statistical Physics and Mechanism of Interaction. *Bulletin of the Chemical Society of Ethiopia*, **37**(1)
- Atrei, A., B. Lesiak-Orlowska, and J. Tóth (2022). Magnetite Nanoparticles Functionalized with Citrate: A Surface Science Study by XPS and ToF-SIMS. *Applied Surface Science*, **602**; 154366
- Baker, H. M., A. M. Massadeh, and H. A. Younes (2009). Natural Jordanian Zeolite: Removal of Heavy Metal Ions from Water Samples Using Column and Batch Methods. *Environmental Monitoring and Assessment*, **157**(1); 319-330
- Bandura, L., M. Białoszewska, S. Malinowski, and W. Franus (2021). Adsorptive Performance of Fly Ash-Derived Zeolite Modified by β -Cyclodextrin for Ibuprofen, Bisphenol A and Caffeine Removal from Aqueous Solutions-Equilibrium and Kinetic Study. *Applied Surface Science*, **562**; 150160
- Bavykina, A., N. Kolobov, I. S. Khan, J. A. Bau, and A. G. J. Ramirez (2020). Metal-Organic Frameworks in Heterogeneous Catalysis: Recent Progress, New Trends, and Future Perspectives. *Chemical Reviews*, **120**(16); 8468-8535
- Behbahani, E. S., K. Dashtian, and M. Ghaedi (2021). Fe₃O₄-FeMoS₄: Promise Magnetite LDH-Based Adsorbent for Simultaneous Removal of Pb(II), Cd(II), and Cu(II) Heavy Metal Ions. *Journal of Hazardous Materials*, **410**; 124560
- Chaudhry, S. A., T. A. Khan, and I. Ali (2016). Adsorptive Removal of Pb(II) and Zn(II) from Water onto Manganese Oxide-Coated Sand: Isotherm, Thermodynamic and Kinetic Studies. *Egyptian Journal of Basic and Applied Sciences*, **3**(3); 287-300
- Chen, G., M. Guan, Z. Yang, F. Mi, Y. Wang, and X. Rao (2024a). High Adsorption Separation Capacity Magnetic MOF-Based Substrate Fe₃O₄@ZIF-67@Ag for Sensitive and Recyclable SERS Detection of Malachite Green in Aquaculture. *Microchemical Journal*, **207**; 112098
- Chen, L. X., J. L. Wang, T. Q. Chai, J. X. Li, P. Li, and F. Q. Yang (2024b). A Hierarchical Porous Fe₃O₄-COOH@H-ZIF-67 Composite as Magnetic Solid-Phase Extraction Adsorbent for Benzimidazole Pesticides. *Microchemical Journal*, **207**; 111870
- Chen, M., N. Wang, X. Wang, Y. Zhou, and L. Zhu (2021). Enhanced Degradation of Tetrabromobisphenol A by Magnetic Fe₃O₄@ZIF-67 Composites as a Heterogeneous Fenton-Like Catalyst. *Chemical Engineering Journal*, **413**; 127539
- Cravillon, J., R. Nayuk, S. Springer, A. Feldhoff, K. Huber, and M. Wiebcke (2011). Controlling Zeolitic Imidazolate Framework Nano and Microcrystal Formation: Insight into Crystal Growth by Time-Resolved In Situ Static Light Scattering. *Chemistry of Materials*, **23**(8); 2130-2141

- Delgado-Marin, J. J., F. Montilla, J. Narciso, and E. V. Ramos-Fernández (2024). Synthesis of Zeolitic Imidazolate Framework 67 Thin Film Coatings on Cobalt Discs. *Thin Solid Films*, **806**; 140515
- Du, X. D., C. C. Wang, J. G. Liu, X. D. Zhao, J. Zhong, Y. X. Li, J. Li, and P. Wang (2017). Extensive and Selective Adsorption of ZIF-67 towards Organic Dyes: Performance and Mechanism. *Journal of Colloid and Interface Science*, **506**; 437–441
- Eltaweil, A. S., S. S. Bakr, E. M. Abd El-Monaem, and G. M. El-Subruiti (2023). Magnetic Hierarchical Flower-Like $\text{Fe}_3\text{O}_4@\text{ZIF-67}/\text{CuNiMn-LDH}$ Catalyst with Enhanced Redox Cycle for Fenton-Like Degradation of Congo Red: Optimization and Mechanism. *Environmental Science and Pollution Research*, **30**(30); 75332–75348
- Emara, M. M., S. T. Hafez, T. E. Khalil, A. E. H. B. Kashyout, A. El-Dissouky, and D. S. El-Sayed (2023). Electronic and Structural Perturbations of Microporous ZIF-67 Nanoparticles and Cr(VI) Molecule During Adsorptive Water Decontamination Unveiled by Experimental and Quantum Computational Investigations. *Journal of Molecular Liquids*, **390**; 123042
- Fu, Q., J. Lou, H. Yuan, R. Zhang, C. Zhang, C. Mo, J. Luo, L. Zha, and P. Wu (2022). In-Situ Grown $\text{ZIF-67}@ \text{Chitosan}$ ($\text{ZIF-67}@ \text{CS}$) for Highly Efficient Removal of Pb(II) from Water. *Journal of Solid State Chemistry*, **316**; 123629
- Gano, Z. S., E. A. Audu, A. A. Osigbesan, A. F. Ade-Ajayi, and J. T. Barminas (2024). Novel Mesoporous Iron Oxide Synthesized from Naturally Occurring Magnetic Sand: A Potential and Promising Catalyst for Chemical Processes. *Inorganic Chemistry Communications*, **159**; 111854
- García, M., S. Collado, P. Oulego, and M. Díaz (2021). Effects of Oxidising Atmosphere on Brewer's Yeast Hydrothermal Treatment and Subsequent Biopolymer Recovery. *Chemical Engineering Journal*, **421**; 127736
- He, X., C. Liu, N. Ju, J. Ji, P. Zhou, and X. Jiang (2026). Microwave Assisted Synthesis of Magnetic $\text{Fe}_3\text{O}_4@\text{TannicAcid}@ \text{ZIF-67}$ for Efficient Removal of Cd(II) and Mn(II): Adsorption Performance and DFT Calculations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*; 139862
- Hou, B. and J. Wu (2020). Halloysite Nanotubes (HNTs) $@ \text{ZIF-67}$ Composites: A New Type of Heterogeneous Catalyst for the Knoevenagel Condensation Reaction. *Dalton Transactions*, **49**(48); 17621–17628
- Huang, J., J. Li, C. Lu, X. Wang, and J. Xu (2025). Magnetic Double-Layer MOF Nanocomposites $\text{Fe}_3\text{O}_4@\text{ZIF-8}@ \text{ZIF-67}$ for Efficient Adsorptive Removal of Organic Dye and Antibiotic. *Journal of Environmental Health Science and Engineering*, **23**(2); 1–17
- Huang, Y., X. Zeng, L. Guo, J. Lan, L. Zhang, and D. Cao (2018). Heavy Metal Ion Removal of Wastewater by Zeolite-Imidazolate Frameworks. *Separation and Purification Technology*, **194**; 462–469
- Jia, T., Y. Gu, and F. Li (2022). Progress and Potential of Metal-Organic Frameworks (MOFs) for Gas Storage and Separation: A Review. *Journal of Environmental Chemical Engineering*, **10**(5); 108300
- Jiang, X., S. Su, J. Rao, S. Li, T. Lei, H. Bai, S. Wang, and X. Yang (2021). Magnetic Metal-Organic Framework ($\text{Fe}_3\text{O}_4@\text{ZIF-8}$) Core-Shell Composite for the Efficient Removal of Pb(II) and Cu(II) from Water. *Journal of Environmental Chemical Engineering*, **9**(5); 105959
- Jiang, X., Y. Zhou, H. Chen, R. Zhang, J. Yu, S. Wang, F. Jiang, H. Bai, and X. Yang (2023). A Novel Hydrangea-Like Magnetic Composite $\text{Fe}_3\text{O}_4@\text{MnO}_2@\text{ZIF-67}$ for Efficient Selective Adsorption of Pd(II) from Metallurgical Wastewater. *Chemosphere*, **344**; 140432
- Kakavandi, B., R. R. Kalantary, A. J. Jafari, S. Nasser, A. Ameri, A. Esrafil, and A. Azari (2015). Pb(II) Adsorption onto a Magnetic Composite of Activated Carbon and Superparamagnetic Fe_3O_4 Nanoparticles: Experimental and Modeling Study. *CLEAN—Soil, Air, Water*, **43**(8); 1157–1166
- Ke, X., X. Song, N. Qin, Y. Cai, and F. Ke (2019). Rational Synthesis of Magnetic $\text{Fe}_3\text{O}_4@\text{MOF}$ Nanoparticles for Sustained Drug Delivery. *Journal of Porous Materials*, **26**(3); 813–818
- Khoshkho, S. M., B. Tanhaei, A. Ayati, and M. Kazemi (2021). Preparation and Characterization of Ionic and Non-Ionic Surfactants Impregnated κ -Carrageenan Hydrogel Beads for Investigation of the Adsorptive Mechanism of Cationic Dye to Develop for Biomedical Applications. *Journal of Molecular Liquids*, **324**; 115118
- Konnerth, H., B. M. Matsagar, S. S. Chen, M. H. Precht, F. K. Shieh, and K. C. W. Wu (2020). Metal-Organic Framework (MOF)-Derived Catalysts for Fine Chemical Production. *Coordination Chemistry Reviews*, **416**; 213319
- Kumar, A., A. K. Singh, and R. Chandra (2021). Recent Advances in Physicochemical and Biological Approaches for Degradation and Detoxification of Industrial Wastewater. In *Emerging Treatment Technologies for Waste Management*. pages 1–28
- Kumar, N., P. P. Kumar, N. Bansal, T. Ahamad, C. Park, H. Ahn, and R. Salunkhe (2025). Polystyrene-MOF-Derived 3D Hierarchical Porous Carbon for High-Performance Supercapacitors. *Chemistry—An Asian Journal*, **20**(4); 202401322
- Lei, Y., H. Yang, J. Xie, Q. Chen, W. Quan, and A. Wang (2023). Synthesis of Strong Magnetic Response ZIF-67 for Rapid Adsorption of Cu^{2+} . *Frontiers in Chemistry*, **11**; 1135193
- Li, S., X. Fan, Z. Chen, and L. Bai (2022). Zeolitic Imidazolate Framework-67 Nanocrystal for High Concentration Cr(VI) Adsorption: A Self-Sacrifice Process. *Desalination and Water Treatment*, **274**; 239–244
- Li, X., X. Gao, L. Ai, and J. Jiang (2015). Mechanistic Insight into the Interaction and Adsorption of Cr(VI) with Zeolitic Imidazolate Framework-67 Microcrystals from Aqueous

- Solution. *Chemical Engineering Journal*, **274**; 238–246
- Liang, X., Y. Wu, G. Chen, P. Wang, Y. Zhang, F. Liu, Y. Qu, Y. Wang, Y. Wu, and L. Li (2026). Fe₃O₄-Modified MOF/-MOF Derivative Composite Materials: Preparation, Modification, and Applications in Wastewater Treatment Applications. *Journal of Physics: Materials*
- Liaskovska, M., T. Tatarchuk, and V. Kotsyubynsky (2025). Structure, Adsorption Properties and Fenton-Like Catalytic Activity of Cobalt Ferrite Nanoparticles Synthesized with *Physalis* Extract. *Physics and Chemistry of Solid State*, **26**(2); 216–230
- Liu, S., W. Zhang, X. Tan, F. Zhao, W. Huang, H. Du, B. A. Goodman, F. Lei, and K. Diao (2018). Performance of a Zeolite Modified with N,N-Dimethyl Dehydroabietylamine Oxide (DAAO) for Adsorption of Humic Acid Assessed in Batch and Fixed Bed Columns. *RSC Advances*, **8**(16); 9006–9016
- Ma, L., X. Zhang, M. Ikram, M. Ullah, H. Wu, and K. Shi (2020). Controllable Synthesis of an Intercalated ZIF-67/EG Structure for the Detection of Ultratrace Cd²⁺, Cu²⁺, Hg²⁺ and Pb²⁺ Ions. *Chemical Engineering Journal*, **395**; 125216
- Mahmoud, S. M., S. H. Ammar, N. D. Ali, F. D. Ali, and Z. H. Jabbar (2024). Visible-Light-Prompted Photocatalytic Degradation of Emerging Contaminants over Facile Constructed ZIF-67/Bi₂₅FeO₄₀ Hybrids. *Journal of Water Process Engineering*, **59**; 104990
- Maryanti, E., W. A. Syafitri, E. Angasa, N. K. A. Bakar, K. C. Sembiring, and G. T. Kadja (2025). Investigation of Congo Red Photodegradation Catalyzed by MOFs ZIF-67@SiO₂ Composite Under Sunlight. *Biointerface Research in Applied Chemistry*, **15**(4); 1–20
- Matatagui, D., A. Sainz-Vidal, I. Gràcia, E. Figueras, C. Cané, and J. M. Saniger (2018). Chemoresistive Gas Sensor Based on ZIF-8/ZIF-67 Nanocrystals. *Sensors and Actuators B: Chemical*, **274**; 601–608
- Moghadam, G., J. Abdi, F. Banisharif, A. Khataee, and M. Kosari (2021). Nanoarchitecturing Hybridized Metal-Organic Framework/Graphene Nanosheet for Removal of an Organic Pollutant. *Journal of Molecular Liquids*, **341**; 117323
- Mostafazadeh, N., A. A. Ghoreyshi, and K. Pirzadeh (2018). Optimization of Solvothermally Synthesized ZIF-67 Metal-Organic Framework and Its Application for Cr(VI) Adsorption from Aqueous Solution. *Iranian Journal of Chemical Engineering*, **15**(4); 27–47
- Nazir, M. A., M. S. Bashir, M. Jamshaid, A. Anum, T. Najam, K. Shahzad, M. Imran, S. S. A. Shah, and A. ur Rehman (2021). Synthesis of Porous Secondary Metal-Doped MOFs for Removal of Rhodamine B from Water: Role of Secondary Metal on Efficiency and Kinetics. *Surfaces and Interfaces*, **25**; 101261
- Nazir, M. A., T. Najam, K. Shahzad, M. A. Wattoo, T. Hussain, M. K. Tufail, S. S. A. Shah, and A. ur Rehman (2022). Heterointerface Engineering of Water Stable ZIF-8@ZIF-67: Adsorption of Rhodamine B from Water. *Surfaces and Interfaces*, **34**; 102324
- Nguyen, M. D., H. V. Tran, S. Xu, and T. R. Lee (2021). Fe₃O₄ Nanoparticles: Structures, Synthesis, Magnetic Properties, Surface Functionalization, and Emerging Applications. *Applied Sciences*, **11**(23); 11301
- Omer, A. M., E. M. Abd El-Monaem, M. M. Abd El-Latif, G. M. El-Subruiti, and A. S. Eltaweil (2021). Facile Fabrication of Novel Magnetic ZIF-67 MOF@Aminated Chitosan Composite Beads for the Adsorptive Removal of Cr(VI) from Aqueous Solutions. *Carbohydrate Polymers*, **265**; 118084
- Paithankar, J. G., S. Saini, S. Dwivedi, A. Sharma, and D. K. Chowdhuri (2021). Heavy Metal Associated Health Hazards: An Interplay of Oxidative Stress and Signal Transduction. *Chemosphere*, **262**; 128350
- Qian, J., F. Sun, and L. Qin (2012). Hydrothermal Synthesis of Zeolitic Imidazolate Framework-67 (ZIF-67) Nanocrystals. *Materials Letters*, **82**; 220–223
- Raj, A., M. G. Galloni, E. Falletta, V. Bortolotto, N. Mila, G. Cerrato, V. F. M. Mezzanotte, M. D. Kurkuri, and C. L. Bianchi (2026). Rapid and Sequential Removal of Polyphe-nols and Heavy Metals from Water by Zeolitic Imidazolate Framework-67 (ZIF-67). *Separation and Purification Technology*; 137783
- Ren, J., A. Meijerink, X. Zhou, J. Wu, G. Zhang, and Y. Wang (2022). In Situ Embedding Synthesis of CsPbBr₃@Ce-MOF@SiO₂ Nanocomposites for High Efficiency Light-Emitting Diodes: Suppressing Reabsorption Losses Through the Waveguiding Effect. *ACS Applied Materials & Interfaces*, **14**(2); 3176–3188
- Sadiq, S., I. Khan, M. Humayun, P. Wu, A. Khan, S. Khan, A. Khan, S. Khan, A. F. Alanazi, and M. Bououdina (2023). Synthesis of Metal-Organic Framework-Based ZIF-8@ZIF-67 Nanocomposites for Antibiotic Decomposition and Antibacterial Activities. *ACS Omega*, **8**(51); 49244–49258
- Sajjadi, S. A., A. Mohammadzadeh, H. N. Tran, I. Anastopoulos, G. L. Dotto, Z. R. Lopičić, S. Sivamani, A. Rahmani-Sani, A. Ivanets, and A. Hosseini-Bandegharai (2018). Efficient Mercury Removal from Wastewater by Pistachio Wood Wastes-Derived Activated Carbon Prepared by Chemical Activation Using a Novel Activating Agent. *Journal of Environmental Management*, **223**; 1001–1009
- Sall, M. L., A. K. D. Diaw, D. Gningue-Sall, A. S. Efremova, and J. J. Aaron (2020). Toxic Heavy Metals: Impact on the Environment and Human Health, and Treatment with Conducting Organic Polymers, A Review. *Environmental Science and Pollution Research*, **27**(24); 29927–29942
- Saxena, V. (2025). Water Quality, Air Pollution, and Climate Change: Investigating the Environmental Impacts of Industrialization and Urbanization. *Water, Air, & Soil Pollution*, **236**(2); 73
- Shearer, G. C., S. Chavan, S. Bordiga, S. Svelle, U. Olsbye, and K. P. Lillerud (2016). Defect Engineering: Tuning the

- Porosity and Composition of the Metal-Organic Framework UiO-66 via Modulated Synthesis. *Chemistry of Materials*, **28**(11); 3749–3761
- Shi, Z., C. Xu, H. Guan, L. Li, L. Fan, Y. Wang, L. Liu, Q. Meng, and R. Zhang (2018). Magnetic Metal Organic Frameworks (MOFs) Composite for Removal of Lead and Malachite Green in Wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **539**; 382–390
- Singh, S., P. N. B. Uppara, R. Varshney, N. Shehata, N. A. Khan, J. Joji, J. Singh, and P. C. Ramamurthy (2024). Facile Synthesis of ZIF-67-Incorporated Electrospun PVA Nanofibers Composite for Efficient Pb(II) Adsorption from Water: Docking and Experimental Studies. *ACS ES&T Water*, **4**(10); 4497–4509
- Song, X., J. Mo, Y. Fang, S. Luo, J. Xu, and X. Wang (2022). Synthesis of Magnetic Nanocomposite $\text{Fe}_3\text{O}_4@\text{ZIF-8}/\text{ZIF-67}$ and Removal of Tetracycline in Water. *Environmental Science and Pollution Research*, **29**(23); 35204–35216
- Tu, N. T. T., T. V. Thien, P. D. Du, V. T. T. Chau, T. X. Mau, and D. Q. Khieu (2018). Adsorptive Removal of Congo Red from Aqueous Solution Using Zeolitic Imidazolate Framework-67. *Journal of Environmental Chemical Engineering*, **6**(2); 2269–2280
- Wang, F., Y. Zheng, X. Wei, D. Lan, J. Zhu, Y. Chen, Z. Wo, and T. Wu (2023). Controlled Synthesis of $\text{Fe}_3\text{O}_4/\text{MnO}_2(310)/\text{ZIF-67}$ Composite with Enhanced Synergistic Effects for the Highly Selective and Efficient Adsorption of Cu(II) from Simulated Copperplating Effluents. *Environmental Research*, **237**; 116940
- Wang, M. L., Z. Zhao, S. Lin, M. Su, B. Liang, and S. X. Liang (2022). New Insight into the Co-Adsorption of Oxytetracycline and Pb(II) Using Magnetic Metal-Organic Frameworks Composites in Aqueous Environment: Co-Adsorption Mechanisms and Application Potentials. *Environmental Science and Pollution Research*, **29**(33); 50177–50191
- Wang, Q., J. Yao, C. Fan, L. Wei, X. Gu, P. Yang, Y. Liu, J. He, A. Peng, K. Qi, and H. Li (2025). Magnetically Active MOF-Based Adsorbent for Efficient Diclofenac Sodium Adsorption. *Scientific Reports*, **15**(1); 43323
- Wei, S., J. Wu, P. Chen, B. Fu, X. Zhu, and M. Chen (2022). Integration of Phosphotungstic Acid into Zeolitic Imidazole Framework-67 for Efficient Methylene Blue Adsorption. *ACS Omega*, **7**(11); 9900–9908
- Wen, T., J. Wang, S. Yu, Z. Chen, T. Hayat, and X. Wang (2017). Magnetic Porous Carbonaceous Material Produced from Tea Waste for Efficient Removal of As(V), Cr(VI), Humic Acid, and Dyes. *ACS Sustainable Chemistry & Engineering*, **5**(5); 4371–4380
- Xie, X., X. Li, and L. Dong (2023). Convenient Synthesis of Co-Base Metal-Organic Frameworks to Effectively Adsorb and Remove Cr(VI) from Aqueous Solution. In *Journal of Physics: Conference Series*, volume 2563. page 012026
- Xue, Y., W. Teng, Y. Chen, Q. Ma, X. Chen, Y. Sun, J. Fan, Y. Qiu, and R. Fu (2022). Amorphous Mn-La Oxides Immobilized on Carbon Sphere for Efficient Removal of As(V), Cd(II), and Pb(II): Co-Adsorption and Roles of Mn Species. *Chemical Engineering Journal*, **429**; 132262
- Yang, W., M. Cheng, Y. Han, X. Luo, C. Li, W. Tang, T. Yue, and Z. Li (2021). Heavy Metal Ions' Poisoning Behavior-Inspired Etched UiO-66/CTS Aerogel for Pb(II) and Cd(II) Removal from Aqueous and Apple Juice. *Journal of Hazardous Materials*, **401**; 123318
- Yuan, S., L. Feng, K. Wang, J. Pang, M. Bosch, C. Lollar, Y. Sun, J. Qin, X. Yang, P. Zhang, and Q. Wang (2018). Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Advanced Materials*, **30**(37); 1704303
- Zargartalebi, R. and Z. Rafiee (2026). One-Pot Synthesis of Polyhydroquinolines Using $\text{GO}/\text{Fe}_3\text{O}_4/\text{ZIF-67}$ Magnetic Nanocatalyst. *Journal of Porous Materials*, **33**(1); 359–372
- Zaynab, M., R. Al-Yahyai, A. Ameen, Y. Sharif, L. Ali, M. Fatima, K. A. Khan, and S. Li (2022). Health and Environmental Effects of Heavy Metals. *Journal of King Saud University-Science*, **34**(1); 101653
- Zhang, H., Y. Mei, F. Zhu, F. Yu, S. Komarneni, and J. Ma (2022). Efficient Activation of Persulfate by $\text{C}/\text{Fe}_3\text{O}_4$ in Visible Light for Tetracycline Degradation. *Chemosphere*, **306**; 135635
- Zhang, Z. H., J. L. Zhang, J. M. Liu, Z. H. Xiong, and X. Chen (2016). Selective and Competitive Adsorption of Azo Dyes on the Metal-Organic Framework ZIF-67. *Water, Air, & Soil Pollution*, **227**(12); 471
- Zhao, G., N. Qin, A. Pan, X. Wu, C. Peng, F. Ke, M. Iqbal, K. Ramachandiraiah, and J. Zhu (2019). Magnetic Nanoparticles@Metal-Organic Framework Composites as Sustainable Environment Adsorbents. *Journal of Nanomaterials*, **2019**(1); 1454358
- Zhao, X., Y. Wang, D. S. Li, X. Bu, and P. Feng (2018). Metal-Organic Frameworks for Separation. *Advanced Materials*, **30**(37); 1705189
- Zhou, L., N. Li, X. Jin, G. Owens, and Z. Chen (2020). A New $\text{nFe}/\text{ZIF-8}$ for the Removal of Pb(II) from Wastewater by Selective Adsorption and Reduction. *Journal of Colloid and Interface Science*, **565**; 167–176
- Zhu, Y., Y. Wang, T. Wang, H. Liu, H. Liu, and M. Zang (2023). One-Step Preparation of Coal-Based Magnetic Activated Carbon with Hierarchically Porous Structure and Easy Magnetic Separation Capability for Adsorption Applications. *Journal of Magnetism and Magnetic Materials*, **569**; 170480