

Synergistic Adsorption-Reduction-Immobilization of Cr(VI) by Fe/Mg-LDH/Biochar: Experimental Validation and DFT/AIMD Mechanistic Insights

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Abstract

Chromium contamination in soil and water is a critical environmental concern due to its high toxicity and mobility. Pristine layered double hydroxides (LDHs) suffer from particle aggregation and narrow pH applicability, while biochar alone exhibits limited immobilization capacity. To overcome these drawbacks, we synthesized an iron-magnesium LDH/biochar composite (FML@BC) via in situ coprecipitation and systematically investigated its synergistic adsorption-reduction-immobilization mechanism for Cr (VI) stabilization. FML@BC achieves a maximum uptake of 138.2 mg/g at pH 5.0, following Langmuir isotherm and pseudo-second-order kinetics, and retains > 80% removal efficiency over a wide pH range of 3.5–7.5, with 82.5% removal efficiency maintained after five regeneration cycles. At a 2% dosage and after 90 days of curing, TCLP-extractable Cr drops from 8.52 to 0.35 mg/L, below the US EPA regulatory limit (5 mg/L). BCR sequential extraction reveals that the mobile Cr fraction (F1 + F2, initially 70%) is largely converted into residual species (F4, 72%), confirming effective long-term immobilization. Density functional theory calculations show stronger binding of Cr (III) (-4.20 eV) than Cr (VI) (-2.85 eV) on the LDH (001) surface, while ab initio molecular dynamics simulations demonstrate that biochar incorporation nearly doubles Cr (III) diffusivity (1.5×10^{-10} m²/s) within the interlayer region. Collectively, these findings establish FML@BC as a promising candidate for in situ chromium remediation via coupled mechanisms, offering a durable and efficient strategy for designing next-generation heavy-metal immobilization agents.

1. Introduction

Heavy metal contamination of soil has become a major global environmental issue, affecting approximately 20 million hectares of land worldwide (Tumolo et al., 2020). Among various heavy metals, chromium (Cr) is of particular concern due to its widespread use in electroplating, leather tanning, dye manufacturing, and metallurgy. In natural environments, Cr mainly exists in two oxidation states: trivalent chromium Cr (III) and hexavalent chromium Cr (VI). Cr (III) typically occurs as cations or insoluble hydroxides, exhibiting low mobility and high stability in soil, and is an essential trace element for human metabolism. In contrast, Cr (VI) predominantly exists as highly soluble oxyanions (CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$), displays strong mobility and wide dispersion in soil-groundwater systems, and can readily migrate to deeper soil layers and groundwater with water flow. More critically, Cr (VI) is far more toxic than Cr (III), with a toxicity that is more than two orders of magnitude higher, and has been classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) (Zhitkovich, 2011). Consequently, Cr (VI) tends to accumulate in organisms through the food chain, posing a serious threat to ecosystems and human health, which underscores the urgent need to develop efficient and sustainable remediation technologies for Cr (VI) contamination (Das et al., 2015; Sable et al., 2024).

In situ stabilization has become one of the primary remediation strategies for heavy metal-contaminated soils, owing to its relatively low cost and minimal site disturbance (Mehdi et al., 2022). The underlying principle involves immobilizing heavy metals in the soil matrix through adsorption, precipitation, ion

exchange, complexation, or redox reactions induced by externally added amendments, thereby reducing their bioavailability and leachability. However, conventional amendments such as lime, phosphate minerals, and pristine biochar generally exhibit limited efficiency in immobilizing anionic heavy metals (e.g., Cr (VI)) and often suffer from strong pH dependence and inadequate long-term stability (Peng et al., 2017; Zhu et al., 2024). Their remediation performance tends to decline markedly under fluctuating environmental conditions, such as acid rain leaching and organic matter degradation (Lyu et al., 2024).

To overcome the above limitations, layered double hydroxides (LDHs) have attracted extensive attention as an emerging class of anionic clay materials, owing to their high anion exchange capacity, large specific surface area, and tunable interlayer chemistry (Wibowo et al., 2025). Among them, iron-containing LDHs additionally possess redox functionality, enabling the reduction of Cr (VI) to less toxic Cr (III) (Usmani et al., 2023). However, pristine LDH nanoparticles tend to aggregate and exhibit poor mechanical stability in soil matrices, resulting in substantial loss of effective surface area and active sites. Biochar, a carbon-rich material derived from pyrolysis of biomass under oxygen-limited conditions, possesses a porous structure, abundant surface functional groups (-COOH, -OH, C = O), and a π -conjugated electron system, enabling it to act as an electron donor for Cr (VI) reduction (Belskaya and Likholobov, 2022). Inspired by the complementary properties of these two materials, the combination of LDHs with biochar to form composites is theoretically expected to utilize the porous scaffold of biochar to inhibit LDH aggregation and facilitate electron transfer, while maintaining the high anion exchange capacity and redox activity of the LDH nanosheets (Fu et al., 2025; Xu et al., 2019).

In recent years, numerous studies have been reported on the application of LDH/biochar composites for Cr (VI) removal. Wang et al. prepared a Ni/Fe-LDH/biochar composite that exhibited an adsorption capacity of approximately 1394.59 mg/kg for Cr (VI) (Wang, W. et al., 2025). Huang et al. respectively investigated the Cr (VI) removal performance of Mg/Al-LDH/biochar composites (Huang et al., 2019). Zubair et al. systematically reviewed the affinity mechanisms of such materials toward anionic pollutants (Zubair et al., 2021b). Collectively, these studies have confirmed that LDH/biochar composites possess favorable Cr (VI) adsorption capability, primarily attributable to interlayer anion exchange and surface complexation (Bar et al., 2024). Despite the foundation laid by these previous works, a comprehensive understanding of the entire pathway from aqueous Cr (VI) capture to soil Cr immobilization remains lacking—particularly regarding the interfacial binding mode of reduced Cr (III), its transformation into residual soil fractions, and its long-term stability under environmental stresses such as acid rain leaching and oxidative perturbation (Bar et al., 2024; Fang et al., 2021; Li, Yan et al., 2026). This knowledge gap critically hinders the translation of promising aqueous-phase adsorption performance into reliable soil remediation outcomes.

To address the aforementioned gaps, this study designed and synthesized an iron-magnesium layered double hydroxide/biochar composite (FML@BC), aiming to construct a remediation system that integrates adsorption, reduction, and immobilization, with biochar serving as the electron donor and dispersing scaffold, and Fe/Mg-LDH functioning as the anion-exchange and structural stabilization unit. The entire process from aqueous-phase adsorption to soil morphology reconstruction was

systematically tracked. The specific research objectives are as follows: (1) to systematically characterize the structural, chemical, and textural properties of the composite and elucidate the interfacial interactions between LDH and biochar; (2) to evaluate its Cr (VI) adsorption performance in aqueous solution under various environmental conditions and quantitatively benchmark it against existing Mg/Fe-LDH/BC systems; (3) to assess its capability for chromium speciation reconstruction and remediation efficiency in Cr-contaminated soil through BCR sequential extraction and TCLP leaching tests; (4) to benchmark its performance against analogous materials reported in the literature (e.g., Mg/Al-LDH/BC and Fe-LDH/BC) under comparable dosages; and (5) to elucidate, at the molecular level, the mechanisms of Cr (VI) reduction, preferential Cr (III) immobilization, and biochar-enhanced Cr (III) diffusion via DFT calculations and AIMD simulations. Through the above investigations, this study aims to address a key scientific question: whether LDH/biochar composites can effectively translate the "adsorption-reduction" of Cr (VI) into the "stabilization-reconstruction" of Cr (III) in soil, thereby achieving long-term remediation with resistance to environmental perturbations. Elucidating this question will not only bridge the gap between aqueous adsorption and soil remediation but also inform the rational design of LDH/biochar composites with durable performance under real-world environmental conditions.

2. Materials and Methods

2.1. Chemicals

All chemical reagents used in this study were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), including $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH, Na_2CO_3 , and $\text{K}_2\text{Cr}_2\text{O}_7$. Deionized water with a resistivity of $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ was used throughout all experiments.

2.2 Preparation of Biochar

Corn straw, collected from Northeast China, was washed thoroughly with deionized water to remove surface impurities and oven-dried at 80°C to constant weight. The dried biomass was ground and sieved through a 100-mesh screen. The resulting powder was placed in a covered ceramic crucible and pyrolyzed in a muffle furnace under N_2 atmosphere at 500°C for 2 h with a heating rate of $10^\circ\text{C}/\text{min}$. After natural cooling to room temperature, the product was sequentially washed with 1 mol/L HCl to remove ash content, rinsed repeatedly with deionized water until the washing solution reached near-neutral pH, and then dried at 100°C . The final material was ground, sieved through a 200-mesh screen, and stored in a sealed container. This material was designated as BC.

2.3 Preparation of Fe/Mg-LDH

Fe/Mg-LDH was synthesized via a conventional coprecipitation method (Aladpoosh and Montazer, 2019; Hasan and Karmakar, 2024). $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, with a Mg/Fe molar ratio of 3:1, were dissolved in 100 mL of deionized water to obtain a mixed salt solution with a total metal ion concentration of approximately 1 mol/L. Separately, an appropriate amount of NaOH and Na_2CO_3 was dissolved in 80 mL of deionized water to prepare a mixed alkali solution, in which the $\text{Na}_2\text{CO}_3/\text{Fe}^{3+}$ molar

ratio was maintained at 2:1. Under N_2 protection, both solutions were simultaneously added dropwise at a rate of approximately 1 mL/min into 200 mL of deionized water under vigorous stirring, while the pH of the system was maintained at 11.0 ± 0.2 using dilute NaOH solution. After complete addition, the slurry was stirred for an additional 30 min, and then aged for 24 h. The resulting precipitate was collected by centrifugation at 5000 rpm for 10 min, washed alternately with deionized water and anhydrous ethanol until free of chloride (tested with 0.1 mol/L $AgNO_3$ solution), dried under vacuum at $60^\circ C$, ground, and sieved through a 200-mesh screen. The product was denoted as FML-3. For comparison, samples with Mg/Fe molar ratios of 2:1 and 4:1 were prepared under identical conditions and designated as FML-2 and FML-4, respectively.

2.4 Preparation of Fe/Mg-LDH/Biochar Composite (FML@BC)

The FML@BC composite was fabricated by in situ growth of LDH nanosheets on the biochar surface. BC was dispersed in the mixed salt solution with a Mg/Fe molar ratio of 3:1 (with a BC-to-target LDH mass ratio of approximately 1:3) and ultrasonicated for 30 min to ensure a uniform suspension. Subsequently, the mixed alkali solution ($NaOH+Na_2CO_3$) was added dropwise to the suspension under vigorous stirring, while the pH was maintained at 11.0 ± 0.2 . The reaction mixture was then transferred to a microwave reactor and heated at $70^\circ C$ under 400 W microwave irradiation for 45 min to promote the in situ nucleation and growth of LDH (Li and Li, 2019). The product was collected by centrifugation, washed to neutrality, dried under vacuum at $60^\circ C$, ground, and sieved through a 200-mesh screen. The resulting material was denoted as FML@BC.

To compare the performance difference between the in-situ grown FML@BC composite and the simply mechanically mixed sample, BC and FML-3 were physically mixed at a mass ratio of 1:3 to prepare a control sample, which was designated as PhysMix.

2.5 Preparation of Calcined LDH (FML-500)

A portion of the FML-3 sample was calcined in a muffle furnace at $500^\circ C$ for 4h under air atmosphere with a heating rate of $10^\circ C/min$. After natural cooling, the resulting Mg-Fe mixed metal oxide was ground and designated as FML-500. This sample served as a control to assess the effect of layered structure collapse on adsorption performance.

2.6 Characterization Methods

The crystalline phases of the prepared materials were analyzed by X-ray diffraction (XRD; Bruker D8 Advance) using Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV and 150 mA, over a 2θ range of $5-80^\circ$ at a scanning rate of $5^\circ/min$. Surface morphology was examined by field-emission scanning electron microscopy (FESEM; JEOL JSM-7900) at an accelerating voltage of 5–10 kV. Transmission electron microscopy (TEM) images were obtained on a JEOL JEF-200 microscope at 200 kV. Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet 7199 spectrometer (Thermo Fisher Scientific) using the KBr pellet method over the range of $400-4000\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . Specific surface area

and pore structure were determined by N_2 adsorption-desorption measurements at -196°C using a Micromeritics ASAP 2460 analyzer. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was derived from the desorption branch using the Barrett-Joyner-Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer with monochromatic Al K α radiation ($h\nu = 1486.6\text{ eV}$), and all spectra were calibrated against the C1s peak at 284.8 eV. Zeta potential measurements were conducted on a Malvern Zetasizer Nano ZS90 as a function of pH (3–11) in 0.001 mol/L NaCl background electrolyte.

2.7 Batch Adsorption Experiments

Effect of pH

The initial pH of the Cr (VI) solution was adjusted to values ranging from 2.0 to 11.0 using 0.1 mol/L HCl or NaOH. Adsorbent (0.05 g) was added to 100 mL of Cr (VI) solution with an initial concentration of 50 mg/L, and the mixture was shaken at $25 \pm 1^\circ\text{C}$ and 500 rpm for 4 h. After filtration through 0.45 μm membrane filters, the residual Cr (VI) concentration in the filtrate was determined by the diphenylcarbazide spectrophotometric method.

Adsorption kinetics

Kinetic experiments were conducted at an initial Cr (VI) concentration of 50 mg/L, pH 5.0, and an adsorbent dosage of 0.5 g/L. Samples were withdrawn at predetermined time intervals (0–480 min) for residual Cr (VI) concentration measurement. The kinetic data were fitted to the pseudo-first-order and pseudo-second-order models, respectively.

Adsorption isotherms

Cr (VI) solutions with initial concentrations ranging from 5 to 500 mg/L were prepared at pH 5.0. Adsorbent (0.5 g/L) was added, and the mixtures were shaken at $25 \pm 1^\circ\text{C}$ for 24 h to reach equilibrium. The equilibrium data were fitted to the Langmuir and Freundlich isotherm models.

Effect of coexisting ions

The influence of coexisting anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- at 10 mmol/L; PO_4^{3-} at 1 mmol/L) and dissolved organic matter (humic acid, 20 mg/L) on Cr (VI) removal efficiency was evaluated under standard adsorption conditions (50 mg/L Cr (VI), pH 5.0, adsorbent dosage 0.5 g/L).

Regeneration experiments

The reusability of FML@BC was evaluated over five consecutive adsorption-desorption cycles. The Cr (VI)-loaded adsorbent was regenerated by washing with 0.1 mol/L NaOH solution, rinsed with deionized water to neutrality, and then reused in the subsequent adsorption cycle.

2.8 Soil Remediation Experiments

Actual contaminated soil was collected from the surface layer (0–20 cm) of agricultural fields developed on loess parent material in southern Gansu Province, China. The soil was air-dried, homogenized, and passed through a 2-mm sieve before use, and its basic physicochemical properties are listed in Table 1. Artificially contaminated soils were prepared by spiking with $K_2Cr_2O_7$ solutions to target Cr (VI) concentrations of 500 mg kg^{-1} , followed by aging for 30 days at 60% of field water capacity with periodic mixing. The measured Cr (VI) concentrations after aging were $442 \pm 15\text{ mg kg}^{-1}$. For the remediation experiments, 100 g of dry soil was mixed with FML@BC at dosages of 1%, 2%, 5%, and 10% (w/w), while equivalent amounts of BC, FML-3, FML-500, and a physical mixture were used as control treatments. The soil-amendment mixtures were incubated in the dark at $25 \pm 1^\circ\text{C}$ with a moisture content of 60%. Samples were collected at 7, 15, 30, 60 and 90 days for analysis of Cr (VI) content, BCR sequential extraction, TCLP.

Table 1
Basic physicochemical properties of the actual contaminated soil.

Parameters	Unit	Value
pH	-	7.24 ± 0.05
EC	$\mu\text{S cm}^{-1}$	285 ± 12
Organic matter	%	1.82 ± 0.08
CEC	cmol kg^{-1}	18.5 ± 0.3
Carbonate	%	3.5 ± 0.2
Clay	%	18.6
Silt	%	61.2
Sand	%	20.2
Water-holding capacity	%	34.5 ± 1.1
Background total Cr	mg kg^{-1}	68.4 ± 2.6
Background Cr (VI)	mg kg^{-1}	< 0.5

In this study, the BCR sequential extraction method was employed for Cr speciation analysis, which sequentially extracted weakly acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions(Fu et al., 2026). TCLP toxicity leaching test was conducted according to the U.S. EPA Method 1311(Li et al., 2024), using acetate buffer solution ($\text{pH} = 2.88 \pm 0.05$) as the extraction fluid at a liquid-to-solid ratio of 20:1 (L/kg), with rotation at $(30 \pm 2)\text{ rpm}$ for $(18 \pm 2)\text{ h}$.

2.9 Computational Methods

In this study, first-principles density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional with Grimme D3(BJ) dispersion correction, as implemented in the Vienna Ab Initio Simulation Package (VASP)(Fezraoui et al., 2026; Jia et al., 2023). The projector augmented wave (PAW) method was employed with a plane-wave cutoff energy of 400 eV. The Fe/Mg-LDH (001) surface was modeled using a 3×3 supercell with a vacuum layer of 15 Å. Adsorption energies (E_{ads}) of Cr (VI) and Cr (III) species were calculated at three states-initial, intermediate, and equilibrium-using the equation $E_{\text{ads}} = E_{\text{total}} - (E_{\text{s}} + E_{\text{adsorbate}})$ (Zou et al., 2024). To evaluate the diffusion behavior of Cr ions within the LDH interlayer region, ab initio molecular dynamics (AIMD) simulations were conducted in the NVT ensemble at 350 K for 10 ps, with temperature controlled by a Nosé-Hoover thermostat(Lan et al., 2025). Furthermore, charge density difference analysis was carried out via a three-step static self-consistent method to elucidate the electron transfer mechanism.

3. Results and discussion

3.1 Characterization of materials

The XRD patterns Fig. 1(a) of BC show two broad peaks at $\sim 24.5^\circ$ and $\sim 43.6^\circ$ corresponding to the (002) and (100) planes of graphitic carbon, indicating amorphous carbon and turbostratic graphite with abundant defect sites that facilitate heterogeneous nucleation of LDH. Among the three LDH samples, FML-3 exhibits the sharpest reflections at (003), (006), and (012) with an interlayer spacing $d_{003} = 0.774$ nm and a well-resolved (110)/(113) doublet, confirming ordered Mg/Fe distribution; the other ratios show notably lower crystallinity(Zubair et al., 2021a). Scherrer calculations yield the largest c-axis crystallite size (~ 25.2 nm) for FML-3, establishing 3:1 as the optimal molar ratio (Chen et al., 2026). The FML@BC composite retains all characteristic LDH peaks, but the (003) peak broadens (FWHM from 0.35° to 0.42°) and the crystallite size decreases to ~ 21.0 nm, which is attributed to strong chemical interactions between biochar surface functional groups (-COOH, -OH) and LDH metal cations that provide abundant nucleation sites and suppress crystallite growth(Huang et al., 2023). The coexistence of BC broad peaks and sharp LDH reflections without any impurities confirms successful composite formation and uniform LDH loading. Upon calcination at 500°C , all LDH diffraction features disappear and are replaced by broad metal oxide peaks, indicating complete collapse of the layered structure into a mixed oxide of MgO and MgFe_2O_4 spinel due to dehydroxylation and interlayer carbonate decomposition.

The FTIR spectra Fig. 1(b) of BC exhibit characteristic bands at 3420 cm^{-1} (O-H stretching), $2920/2854\text{ cm}^{-1}$ (aliphatic C-H), 1705 cm^{-1} (carboxyl/carbonyl C = O), 1612 cm^{-1} (aromatic C = C), and 1092 cm^{-1} (C-O-C/C-OH), confirming abundant oxygen-containing groups that provide both adsorption sites and chemical nucleation centers for LDH growth. FML-3 shows typical LDH absorptions: a broad band at $\sim 3450\text{ cm}^{-1}$ for hydroxyl groups and interlayer water, a sharp peak at 1365 cm^{-1} for interlayer CO_3^{2-} antisymmetric stretching (ν_3), and bands at 558 and 448 cm^{-1} assigned to M-O-M lattice vibrations and

M-O stretching, respectively, substantiating the metal-oxygen framework(Wang, Z. et al., 2025). The FML@BC composite retains all characteristic peaks of both components, evidencing successful combination. Notably, the CO_3^{2-} band shifts to 1370 cm^{-1} upon compositing, indicating altered chemical environment of interlayer carbonate due to interfacial M-O-C bonding between BC surface functional groups (-COOH, -OH) and edge metal ions (Mg^{2+} , Fe^{3+}), which modulates the vibrational energy level via electronic effects. Meanwhile, the relative intensity of the C = O band at 1705 cm^{-1} decreases, suggesting coordination of some oxygenated groups with LDH metal cations. These findings collectively confirm strong interfacial chemical coupling rather than mere physical mixing between FML-3 and BC, consistent with the reduced crystallite size observed in XRD(Boostani et al., 2024; Hu et al., 2025).

The N_2 adsorption-desorption isotherms and pore structure parameters of the different samples are presented in Fig. 1(c) and the corresponding data are summarized in Table 2. BC exhibit a mixed-type isotherm with an H3 hysteresis loop, characteristic of micro-mesoporous carbon with slit-shaped pores arising from platelet stacking; BC shows a BET surface area of $185.2\text{ m}^2/\text{g}$ with a 76.9% micropore contribution and a total pore volume of $0.212\text{ cm}^3/\text{g}$. In contrast, pure FML-3 displays a much lower surface area due to its compact layered structure. The FML@BC composite presents an intermediate BET surface area of $142.6\text{ m}^2/\text{g}$, but its total pore volume ($0.324\text{ cm}^3/\text{g}$) is approximately 72% higher than the linearly weighted predicted value, revealing substantial generation of nanoscale interfacial gaps (3–15 nm) during in-situ LDH growth(Yang et al., 2022). This enhancement arises from three effects: non-compact stacking of LDH nanosheets on BC creating extra void spaces, restricted LDH crystallite growth due to abundant nucleation sites leading to looser particle packing, and preservation of LDH interlayer mesoporosity alongside partial coverage of BC micropores(Chergui et al., 2026; Pan et al., 2025). Upon calcination at 500°C , the collapsed LDH structure undergoes sintering and aggregation, resulting in a marked decrease in both surface area and pore volume. These pore structure characteristics provide critical evidence for elucidating the composite formation mechanism and the structure-activity relationship governing subsequent adsorption performance.

The pore size distribution curves Fig. 1(d) show that BC exhibits a bimodal distribution of micropores (< 2 nm) and narrow mesopores (2–5 nm), consistent with its high micropore contribution, while FML-3 displays only a dispersed mesoporous pattern (2–50 nm) with negligible microporosity. In FML@BC, micropores largely attenuate or disappear, whereas mesopores in the 3–15 nm range increase substantially, attributed to in-situ LDH nanosheet coverage of micropores and the formation of abundant interfacial gaps from loose, non-compact LDH stacking. This mesopore enrichment, which aligns with the ~ 72% excess total pore volume, indicates pore reconstruction-partial sacrifice of microporosity to significantly enhance mesoporosity. Upon calcination, FML-500 loses its mesoporous features and transforms into a broad macropore distribution, reflecting structural coarsening due to sintering and collapse of the layered framework.

Table 2
N₂ adsorption-desorption isotherms and pore structure parameters of BC, FML-3, FML@BC and FML-500.

Samples	BET (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)
BC	185.2	4.58	0.212
FML-3	72.4	10.39	0.188
FML@BC	142.6	9.09	0.324
FML-500	119.5	8.23	0.246

3.2 Aqueous-Phase Cr (VI) Adsorption Performance

The pH-dependent Cr (VI) removal Fig. 2(a) reveals that BC removal decreases with increasing pH, with maximum efficiency at pH 3 owing to protonated surface oxygen groups attracting HCrO₄⁻, while deprotonation at higher pH enhances electrostatic repulsion. In contrast, FML-3 samples show a bell-shaped trend with optimal removal (88–92%) at pH 5–6, attributed to favorable surface positive charge and low-energy exchange of monovalent HCrO₄⁻ in the acidic range, but competition from OH⁻ and conversion to divalent CrO₄²⁻ reduce removal above pH 6 (Alghamdi et al., 2023). The FML@BC composite exhibits superior broad-pH performance (> 80% from pH 3.5 to 7.5) and reaches 96.5% at pH 5.0, benefiting from synergistic contributions: LDH provides anion-exchange sites and Fe³⁺/Fe²⁺ redox pairs, while BC enhances adsorption via electrostatic interactions and π - π electron systems, with its buffering capacity mitigating structural degradation of LDH under extreme pH. In comparison, calcined FML-500 loses layered structure and anion-exchange capacity, showing only ~ 55% removal, and the physical mixture (PhysMix) reaches only 79%, confirming that in-situ chemical coupling yields substantially stronger interfacial synergy than physical mixing alone. These results demonstrate that the broad pH effectiveness of FML@BC originates from the combined action of LDH layered structure, BC conductive/buffering properties, and interfacial chemical bonding between them.

The effect of initial Cr (VI) concentration (10–500 mg·L⁻¹) on removal efficiency is shown in Fig. 2(b). BC removal declines sharply from 96% to 8% due to its limited surface oxygen groups lacking interlayer exchange sites (Chen et al., 2021). The three LDH samples exhibit nearly identical concentration-dependent behavior, maintaining 77–98% at low concentrations and still 26–30% at 500 mg·L⁻¹, substantially outperforming BC through dual mechanisms of interlayer anion exchange and surface complexation at edge M-OH sites, with negligible Mg/Fe ratio effect. FML@BC achieves the best performance across all concentrations, with 99% at 10 mg·L⁻¹ and 43% at 500 mg·L⁻¹, far exceeding the physical mixture (22% at 500 mg·L⁻¹). This superiority is ascribed to the mesoporous BC skeleton that ensures high dispersion of LDH nanosheets, avoiding site waste from aggregation, and the M-O-C interfacial bonds that enhance structural stability, preserving more active sites under high concentrations. In contrast, calcined FML-500 shows the lowest efficiency (only 18% at 500 mg·L⁻¹) due

to complete collapse of the layered structure and loss of anion-exchange capacity, leaving only limited surface adsorption on metal oxides.

The effect of adsorbent dosage (0.05-10 g/L) on Cr (VI) removal is shown in Fig. 2(c). For all materials, removal efficiency increases sharply at low dosage and then plateaus, as active sites become progressively saturated and the concentration gradient driving mass transfer diminishes. Notably, FML@BC achieves 95% removal at 0.5 g/L and stabilizes at ~ 99% beyond 1 g/L, outperforming BC (~ 45%), FML-3 (~ 92%), and the physical mixture (~ 80%) by margins of 54%, 7%, and 19%, respectively (Cheng et al., 2026). This superior performance stems from the in-situ chemical coupling: the mesoporous BC skeleton exerts a spatial confinement effect that disperses LDH nanosheets onto pore surfaces, effectively preventing face-to-face stacking and thus maximizing exposure of interlayer exchange sites and edge M-OH coordination sites. Meanwhile, the covalent M-O-C interfacial bonds between BC oxygen groups and LDH metal cations not only enhance structural stability but also modulate the local chemical environment of interlayer CO_3^{2-} via electronic induction, lowering the energy barrier for Cr (VI) oxyanion exchange. The pristine LDH samples reach 87–93% removal but suffer from aggregation that shields interlayer channels, while the physical mixture lacks chemical bridging and shows only additive contributions, with its micropores partially blocked by LDH particles. BC alone exhibits the lowest plateau removal (~ 45%) due to its reliance on limited surface groups and π - π interactions without interlayer confinement (Zhang et al., 2024). Calcined FML-500 retains only ~ 57% removal, as the collapsed layered structure eliminates anion-exchange capacity, leaving only surface adsorption on MgO/MgFe₂O₄ mixed oxides.

The influence of coexisting species (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and HA) on Cr (VI) removal by FML@BC is shown in Fig. 2(d), with the inhibitory sequence following PO_4^{3-} (58.85%) > HCO_3^- (75.47%) > SO_4^{2-} (83.13%) > HA (87.44%) > Cl^- (94.93%) $\approx$ NO_3^- (94.99%). Cl^- and NO_3^- exert negligible effects due to their monovalent weak coordination, while SO_4^{2-} shows notable competition via divalent electrostatic attraction. The stronger inhibition of HCO_3^- arises from dual effects: direct exchange competition and hydrolysis-induced pH rise that converts Cr (VI) to CrO_4^{2-} , increasing the exchange barrier, along with OH^- competition. PO_4^{3-} exhibits the strongest suppression, attributed to its trivalent charge and formation of stable inner-sphere complexes at edge M-OH sites, thereby blocking both anion exchange and surface complexation (Wang et al., 2024). HA causes only mild interference through steric hindrance and surface coverage. Notably, removal efficiency remains ~ 60% even in the presence of PO_4^{3-} , demonstrating the good anti-interference capability of FML@BC in complex water matrices (Xiong et al., 2024; Zubair et al., 2021b).

3.3 Studies on adsorption kinetics and isotherms

The kinetic fitting results Fig. 3(a,b) demonstrate that the pseudo-second-order model ($R^2 = 0.999$) provides a significantly better description than the pseudo-first-order model ($R^2 = 0.976$ – 0.981) for all tested samples, and the equilibrium adsorption capacities ($q_{\text{eq,cal}}$) derived from the pseudo-second-order

model are in good agreement with the experimental values. This confirms that chemisorption governs the overall adsorption kinetics, with the adsorption rate controlled by electron exchange or coordination interactions between the adsorbent and Cr (VI) oxyanions, rather than by physical mass transfer. In terms of adsorption capacity, FML@BC reaches 68.40 mg/g, which is 2.1-fold that of BC (32.53 mg/g) and comparable to that of FML-3 (67.39 mg/g)(Tran et al., 2019). The physical mixture (PhysMix) exhibits an intermediate q_e of 55.34 mg/g-higher than BC but lower than both FML-3 and FML@BC- indicating that simple physical mixing offers only marginal enhancement over pristine BC and falls far short of the synergistic effect achieved through the chemical coupling in FML@BC. Notably, although FML@BC and FML-3 possess comparable equilibrium capacities (68.40 vs. 67.39 mg/g), FML@BC exhibits markedly higher removal efficiency (~ 99%) than FML-3 (~ 92%) and PhysMix (~ 80%) due to enhanced site accessibility. The biochar scaffold alleviates LDH aggregation, exposing more interlayer and edge sites within the kinetic timeframe, whereas active sites in FML-3 and PhysMix remain largely buried(Zhang et al., 2021; Zhao et al., 2025). The M-O-C interfacial bonding in FML@BC further stabilizes the composite architecture, ensuring that chemisorption sites are well preserved and readily accessible throughout the adsorption process. Kinetics analysis corroborates this interpretation: the pseudo-first-order rate constant k_1 of FML@BC (0.17 min^{-1}) is 1.7-fold that of FML-3 (0.098 min^{-1}) and 4.3-fold that of BC (0.040 min^{-1}), confirming that the mesoporous channels (3–15 nm) of the biochar support shorten the diffusion pathway of Cr (VI) to the interlayer active sites and reduce mass-transfer resistance, thereby significantly enhancing the apparent adsorption rate. The detailed kinetic parameters for all samples are summarized in Table 3.

Table 3
Kinetic parameters of BC, FML-3, FML@BC and FML-500.

Model	Parameters	BC	FML-3	FML@BC	PhysMix
Pseudo-First Order	q_e	29.57	65.19	69.89	52.66
	k_1	0.040	0.120	0.170	0.098
	R^2	0.977	0.978	0.981	0.976
Pseudo-Second Order	q_e	32.53	67.39	68.40	55.34
	k_1	0.002	0.003	0.003	0.004
	R^2	0.999	0.999	0.999	0.999

Table 4
Adsorption isotherms parameters of BC, FML-3, FML@BC and FML-500.

Model	Parameters	BC	FML-3	FML@BC	PhysMix
Langmuir	q_e	45.6	108.5	138.2	81.1
	k_l	0.006	0.006	0.003	0.007
	R^2	0.993	0.999	0.999	0.998
Freundlich	k_f	2.98	7.40	5.13	6.55
	$1/n$	0.55	0.58	0.72	0.55
	R^2	0.946	0.972	0.993	0.963

The isotherm fitting results Fig. 3(c,d) show that the Langmuir model ($R^2 = 0.999$) provides a better fit than the Freundlich model ($R^2 = 0.993$) for all samples. FML@BC achieves a maximum monolayer adsorption capacity of 138.2 mg/g, surpassing BC (45.6 mg/g), FML-3 (108.5 mg/g), and PhysMix (81.1 mg/g). The enhancement is attributed to the spatial confinement effect of the BC mesoporous scaffold, which promotes high dispersion of LDH nanosheets, fully exposing interlayer exchange sites and edge M-OH coordination sites, while the M-O-C interfacial bonds stabilize the composite structure (Zhang et al., 2021). The detailed adsorption isotherms parameters for all samples are summarized in Table 4.

3.4 Soil Stabilization Performance

The reusability of BC, FML-3, and FML@BC was evaluated over five consecutive cycles Fig. 4(a). Although all samples showed a progressive decline in Cr (VI) removal efficiency with increasing cycle number, the extent of decrease varied markedly. FML@BC maintained 82.5% removal after five cycles, down from 95.2% initially, corresponding to a retention rate of 86.7%, substantially outperforming FML-3 (90.6% to 61.5%, retention 67.9%) and BC (45% to 10.5%, retention 23.3%). The superior cyclic stability of FML@BC is attributed to the in-situ chemical coupling that establishes M-O-C interfacial bonding, which strengthens the adhesion between LDH nanosheets and the BC support, effectively suppressing exfoliation and aggregation during adsorption-desorption cycles. Additionally, the mesoporous scaffold of BC provides physical confinement protection that mitigates the leaching of layer metal cations. In contrast, the poorer stability of FML-3 arises from layer stacking and partial structural degradation upon repeated use, leading to a reduction in interlayer exchange sites, while the sharp decline of BC results from irreversible consumption of surface oxygen-containing groups and the difficulty of regenerating physically dominated adsorption sites (Wibowo et al., 2025).

The TCLP leaching test Fig. 4(b) evaluated the immobilization efficiency of different materials toward soil Cr (VI). The untreated soil exhibited a leachate concentration of 8.52 mg/L, far exceeding the regulatory threshold. All amendments significantly reduced the leached Cr (VI) concentration. Under the same conditions, the immobilization capacity followed the order: FML@BC > FML-500 > FML-3 >

PhysMix > BC. FML@BC showed the best performance, reducing the leachate concentration from 8.52 to 0.78 mg/L at a 2% dosage after 30 days of curing, corresponding to an immobilization efficiency of 90.8% (Li, Yingchao et al., 2026). This was markedly superior to FML-3 (3.21 mg/L), BC (5.83 mg/L), and PhysMix (4.10 mg/L) under the same conditions, confirming the indispensable contribution of in-situ chemical coupling. Dosage experiments (1–10%) revealed a progressive decrease in leachate concentration from 1.82 to 0.31 mg/L (immobilization efficiency increasing from 78.6% to 96.4%). Moreover, extending the curing time from 30 to 90 days at a 2% dosage further lowered the concentration to 0.35 mg/L, indicating sustained stabilization without desorption rebound. These results demonstrate that FML@BC exhibits notable dose-dependent and long-term immobilization performance, suggesting promising potential for soil Cr (VI) remediation.

The BCR sequential extraction procedure was employed to evaluate the fractionation of Cr in soil after treatment with different materials Fig. 4(c). In untreated soil, the acid-extractable (F1) and reducible (F2) fractions accounted for 69.6% of total Cr, indicating that Cr predominantly existed in bioavailable forms with high environmental risk (Zhu et al., 2025). Upon amendment addition, all treatments showed a pronounced decrease in F1, and F2 fractions accompanied by a significant increase in the residual fraction (F4), demonstrating effective transformation of Cr from labile to stable forms. The immobilization efficiency followed the order: FML@BC > FML-500 > FML-3 > PhysMix > BC, consistent with the TCLP results. Specifically, after 30 days with 2% FML@BC, F1 decreased from 41.8% to 12.3%, while F4 increased substantially from 12.2% to 52.7%, achieving an immobilization efficiency of 87.7%; at a 10% dosage, F1 further dropped to only 5% and F4 rose to 71.7%, indicating a clear dose-dependent effect. Extending the curing time to 90 days at 2% dosage further reduced F1 to 2.8% and elevated F4 to 77%, confirming the sustained long-term stabilization capability of the composite (Li, Yingchao et al., 2026; Zhou et al., 2025). Notably, FML-500 exhibited a lower F4 proportion (40%) than FML@BC (52.7%) but still outperformed FML-3 (28.8%), supporting the mechanism that the calcination-derived MgO/MgFe₂O₄ mixed oxides facilitate Cr species transformation via surface precipitation and alkaline-induced reduction in the soil solid phase. The in-situ chemically coupled FML@BC, leveraging the synergistic interplay of LDH interlayer exchange, BC electron transfer, and surface complexation, efficiently converts labile Cr into the residual fraction, thereby substantially reducing the environmental mobility and risk of soil Cr.

Figure 4(d) illustrates the evolution of Cr stabilization efficacy in soil across different materials over a 90-day incubation period. All treatment groups exhibited a biphasic pattern characterized by a rapid initial decline followed by a gradual plateau. Among all amendments, FML@BC demonstrated the optimal performance: the soil Cr concentration decreased from 442 mg/kg to 24 mg/kg at 30 d (immobilization efficiency of 94.6%), and further to 5 mg/kg at 90 d (immobilization efficiency of 98.9%), substantially outperforming FML-3 (38 mg/kg), PhysMix (90 mg/kg), FML-500 (140 mg/kg), and BC (185 mg/kg) at equivalent dosage. The sustained enhancement in stabilization capacity is ascribed to the synergistic contributions of (i) rapid Cr (VI) sequestration via LDH interlayer anion exchange, (ii) electron transfer-mediated reduction enabled by the conductive BC backbone, and (iii) long-term hydrochemical stability of the composite architecture. The superior performance of FML-500 over BC and PhysMix is

attributable to the surface hydroxyl species generated during hydration of $\text{MgO/MgFe}_2\text{O}_4$, which facilitate surface precipitation and immobilization of Cr. In contrast, BC alone reduced the soil Cr concentration to only 185 mg/kg at 90 d (immobilization efficiency of 58.1%), indicating that pristine biochar lacks deep-seated chemical immobilization capacity and poses a potential risk of re-mobilization (Liu et al., 2024). Collectively, FML@BC reduced the soil Cr concentration to 5 mg/kg over the 90-d incubation period, well below the toxicity characteristic leaching procedure (TCLP) regulatory threshold, thereby substantiating its long-term, durable remediation capability for Cr-contaminated soils (Lin et al., 2025).

3.5 Mechanistic Insights from DFT and AIMD Simulations

Figure 5(a) presents the periodic DFT slab model of the FML-3 (001) crystal surface. The (001) plane is the preferentially exposed growth facet of LDH, featuring a uniform distribution of abundant unsaturated coordination hydroxyl (-OH) groups, which serve both as active sites with lone-pair electrons for coordination and as the primary interface bearing the positive layer charge. Figure 5(b) displays the LDH interlayer/interfacial model incorporating a hydration layer, constructed for AIMD diffusion simulations.

Figure 5(c) shows the evolution of adsorption energies for Cr (VI) and Cr (III) at the initial, intermediate, and equilibrium stages. Both species exhibit negative adsorption energies throughout all stages, confirming that their binding onto the LDH surface is thermodynamically spontaneous. The adsorption energy of Cr (VI) progressively decreases from -1.45 eV to -2.15 eV (intermediate) and -2.85 eV (equilibrium), indicating a transition from outer-sphere electrostatic association/hydrogen-bonding physisorption to inner-sphere coordination chemisorption at layer edges or defect sites (Zhang et al., 2025). For Cr (III), the adsorption energy drops significantly from -2.10 eV to -3.20 eV and -4.20 eV. It must be emphasized that this trend is not attributable to electrostatic attraction-on the contrary, the LDH layers carry a permanent positive charge due to isomorphous substitution, which imposes a Coulombic repulsion on the cationic Cr (III) aqua species.

The exceptionally strong adsorption of Cr (III) originates from its distinctive interfacial chemistry: once $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ overcomes the initial repulsive barrier and approaches the layer surface, the coordinated water molecules undergo rapid deprotonation and irreversible ligand exchange with surface -OH groups, forming stable inner-sphere Cr-O bonds (Tang et al., 2022). Concurrently, Cr (III) exhibits a strong tendency for hydrolysis and polymerization, leading to in-situ formation of a $\text{Cr}(\text{OH})_3$ surface precipitate under the alkaline microenvironment of the layer. The enthalpic contributions from chemical bonding and precipitation reactions (mixed covalent/ionic bonds) far outweigh the purely electrostatic potential, ultimately yielding a thermodynamic driving force as high as -4.20 eV at the equilibrium stage.

Figure 5(d) illustrates the time evolution of the system temperature during the AIMD simulations, performed under the NVT ensemble with a Nose-Hoover thermostat set at 350 K. The system reaches the target temperature within less than 1 ps, and over the subsequent 10-ps trajectory the temperature fluctuation is strictly controlled within ± 5 K, confirming that the system has achieved sufficient thermal equilibration (Gao et al., 2018). Consequently, the extracted MSD curves and derived diffusion

coefficients are statistically robust and kinetically representative, free from pseudo-diffusion artefacts caused by thermal drift. Figure 5(e) compares the MSD profiles and the corresponding diffusion coefficients (D) for three systems: Cr (VI)-LDH gives $D = 3.5 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, Cr (III)-LDH gives $D = 8.2 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, and Cr (III)-FML@BC gives $D = 1.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (Hu et al., 2021). The extremely low diffusivity of Cr (VI) is readily understandable: the CrO_4^{2-} anion is strongly electrostatically attracted by the positively charged LDH layers, and its relatively large ionic radius suffers from severe steric hindrance within the narrow interlayer galleries, thus being essentially confined near the exchange sites. For Cr (III), however, the Coulombic repulsion from the positively charged layers is primarily relevant along the out-of-plane direction, where it acts as the initial energy barrier; once inside the interlayer galleries, however, lateral migration is largely screened by abundant water molecules and anions, resulting in reduced frictional resistance and hence higher diffusivity. Upon introduction of the biochar substrate (FML@BC), the diffusion coefficient of Cr (III) nearly doubles ($1.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$), which is attributed to the porous carbon skeleton of BC providing detour diffusion channels that bypass the narrow LDH interlayers, while its conductive nature imposes a shielding effect on the local electric field of LDH, effectively mitigating the electrostatic confinement and kinetically facilitating the transport of Cr (III) toward deeper stable sites.

Figure 5(f) presents the charge density difference map with isosurface colour mapping, visually displaying the electron redistribution at the adsorption interface. Clear physical evidence shows significant electron depletion (blue/electron-deficient regions) around the lattice oxygen atoms on the LDH surface, accompanied by pronounced electron accumulation (yellow/electron-rich regions) around the adsorbed Cr ions. Quantitative Bader charge analysis yields a net charge transfer of approximately $0.45 e^-$, which is far beyond the typical magnitude for physisorption (usually $< 0.05 e^-$), conclusively demonstrating the formation of a significantly polar covalent coordination bond between Cr and surface O atoms (Yin et al., 2024). This directional electron flow not only accounts for the substantial negative shift in adsorption energy at the electronic level, but also provides direct structural evidence for the electron donor source that may facilitate the reduction of Cr (VI) to Cr (III) within the layers. Figure 5(g) quantitatively compares the net charge transfer for Cr (VI) and Cr (III) upon equilibrium adsorption on the FML-3 (001) surface: Cr (VI) displays a range of $0.6\text{--}0.9 e^-$, whereas Cr (III) is consistently centred at $0.8\text{--}0.9 e^-$ (Qi et al., 2022). The charge transfer originates from electron migration from surface lattice oxygen to the empty orbitals of Cr ions, and its magnitude directly reflects the covalency of the Cr-O bond. The higher and more concentrated charge transfer for Cr (III) indicates the formation of stronger inner-sphere covalent coordination bonds with surface -OH groups compared to Cr (VI), consistent with its more negative adsorption energy.

4. Conclusions

(1) FML@BC composite was successfully fabricated, with LDH nanosheets uniformly grown on biochar via M-O-C interfacial bonding, generating abundant mesopores (3–15 nm), a BET surface area of 142.6

m²/g, and a total pore volume ~ 72% higher than the physical mixture, while preserving the intact LDH layered structure.

(2) Aqueous adsorption tests showed that FML@BC achieves > 80% removal over a broad pH range (3.5–7.5), with a maximum Langmuir capacity of 138.2 mg/g, governed by pseudo-second-order chemisorption. The interference sequence of coexisting ions is $\text{PO}_4^{3-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{HA} > \text{Cl}^- \approx \text{NO}_3^-$, yet ~ 60% removal remains even in the presence of PO_4^{3-} , confirming good anti-interference ability.

(3) In soil remediation, at a 2% dosage, TCLP-leachable Cr decreased from 8.52 to 0.35 mg/L (immobilization efficiency 90.8%). BCR speciation analysis revealed that the mobile fraction (F1 + F2) dropped from 70% to < 15%, while the residual fraction (F4) increased from 12.2% to 77% over 90 days, indicating a highly efficient and time-dependent transformation of Cr from labile to stable forms.

(4) DFT and AIMD calculations elucidated that Cr (VI) binds via interlayer exchange and edge coordination, whereas Cr (III), overcoming electrostatic repulsion, forms irreversible inner-sphere covalent bonds with surface -OH groups and induces surface precipitation, with an adsorption energy of -4.20 eV. Biochar incorporation nearly doubles the diffusivity of Cr (III) by providing bypass channels and shielding the local electric field, thus promoting deeper immobilization.

Collectively, FML@BC achieves efficient Cr (VI) adsorption, reduction, and long-term stabilization through the synergistic interplay of LDH interlayer exchange, biochar electron transfer, interfacial chemical coupling, and subsequent immobilization. The composite exhibits excellent cyclic stability and resistance to environmental fluctuations, offering a viable and sustainable approach for the remediation of chromium-contaminated soils.

Declarations

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contribution

Jianfang Fu: Conceptualization, Data curation, Methodology, Writing-review & editing, Writing -original draft; Zexu Wang: Conceptualization, Investigation, Methodology, Writing-review & editing; Yuhong Yang: Methodology, Resources, Supervision, Writing-original draft; Xiaoyan Wang: Investigation, Supervision

Validation, Visualization; Yunfeng Xu: Funding acquisition, Investigation, Methodology, Project administration.

Data availability

Data will be made available on request.

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Figures

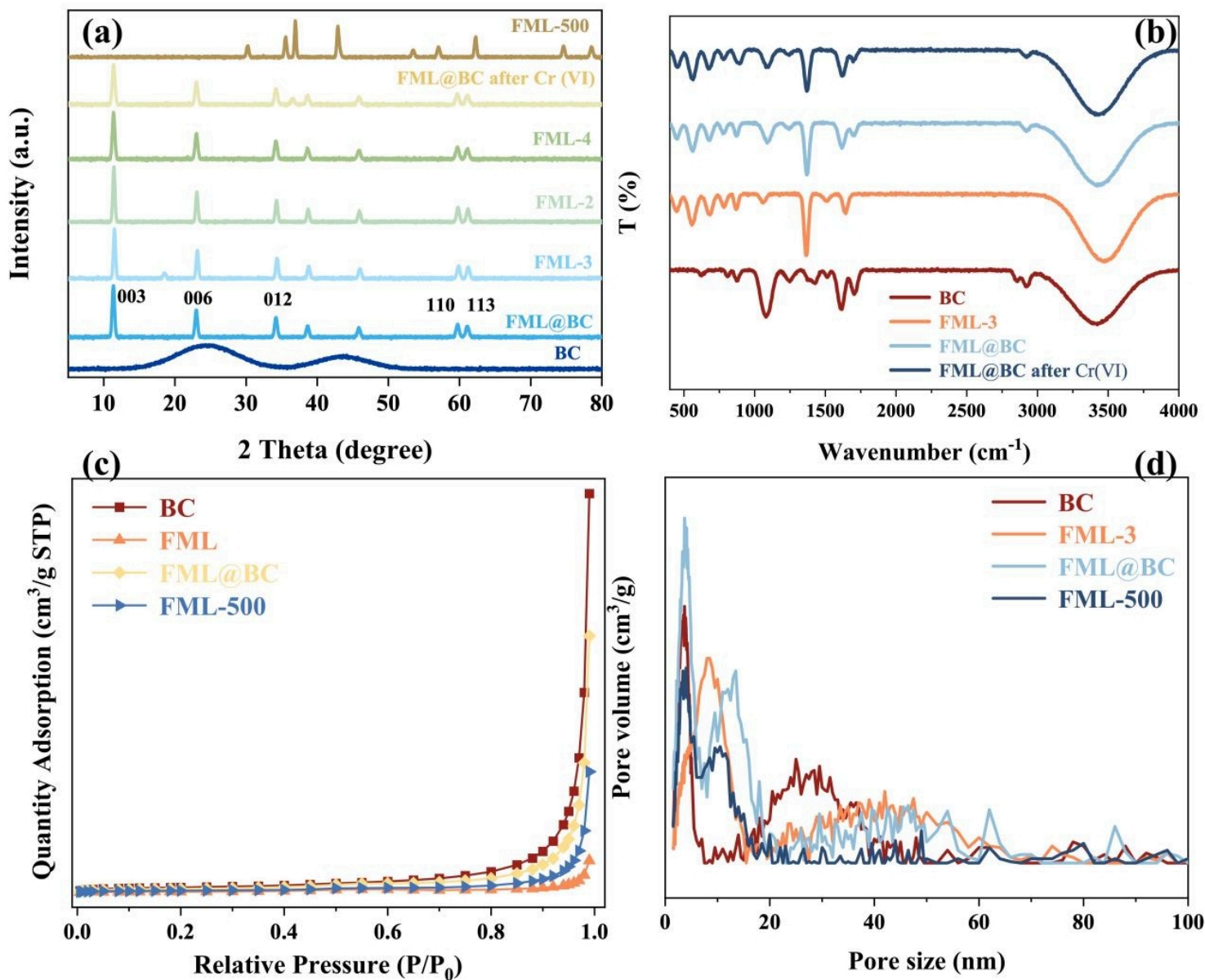


Figure 1

(a) XRD patterns of BC, FML-2, FML-3, FML-4, FML-500, and FML@BC before and after Cr (VI) adsorption; (b) FTIR spectra of BC, FML-3, FML@BC, and FML@BC after Cr (VI) adsorption. (c) N₂ adsorption-

desorption isotherms of BC, FML-3, FML@BC, and FML-500; (d) Pore size distribution curves of BC, FML-3, FML@BC, and FML-500.

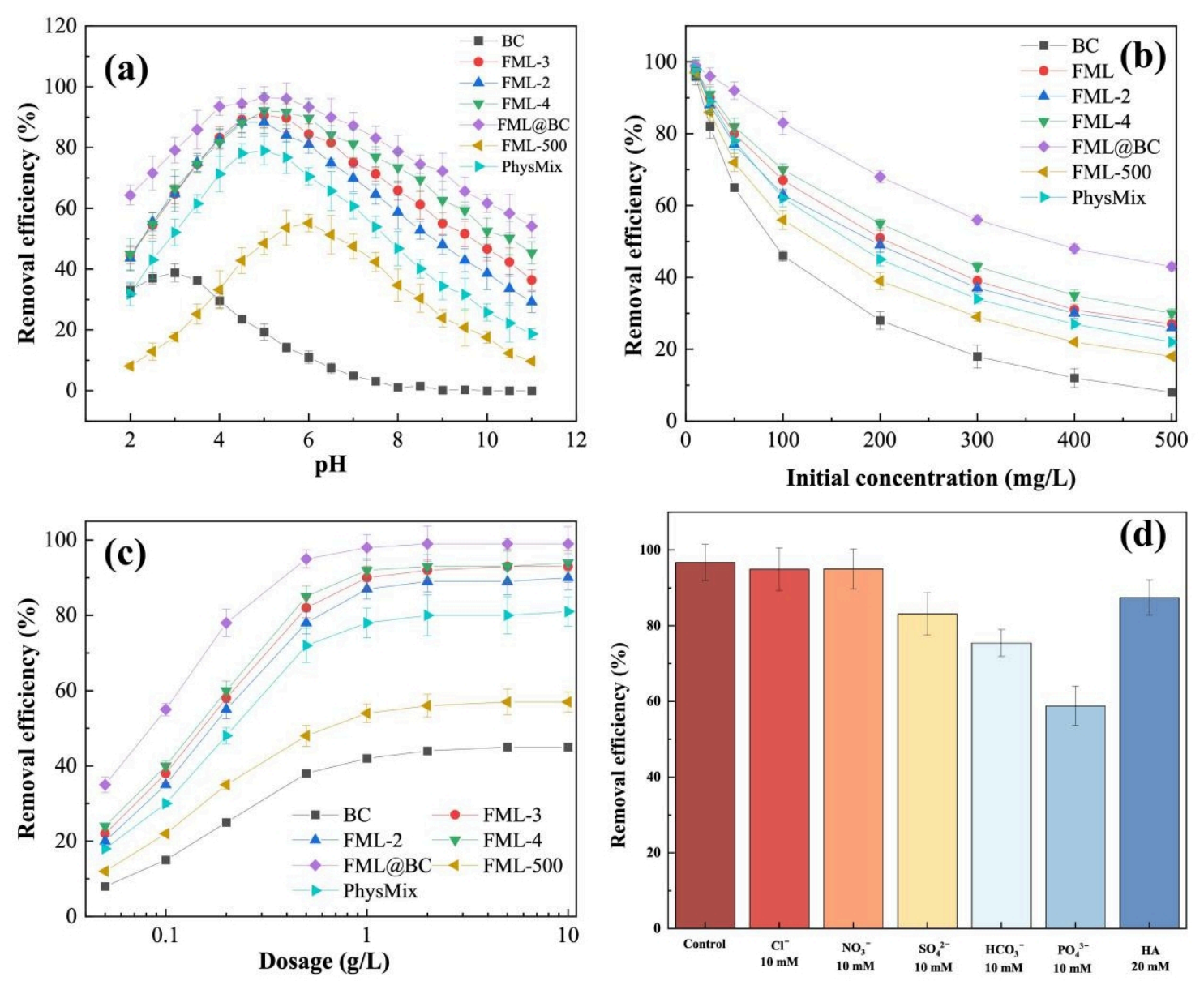


Figure 2

(a) Effect of pH on the adsorption performance of BC, FML-2, FML-3, FML-4, FML-500, FML@BC, and PhysMix; (b) Effect of initial Cr (VI) concentration on the adsorption performance of BC, FML-2, FML-3, FML-4, FML-500, FML@BC, and PhysMix; (c) Effect of adsorbent dosage on the adsorption performance of BC, FML-2, FML-3, FML-4, FML-500, FML@BC, and PhysMix; (d) Effect of coexisting ions on the adsorption performance of FML@BC.

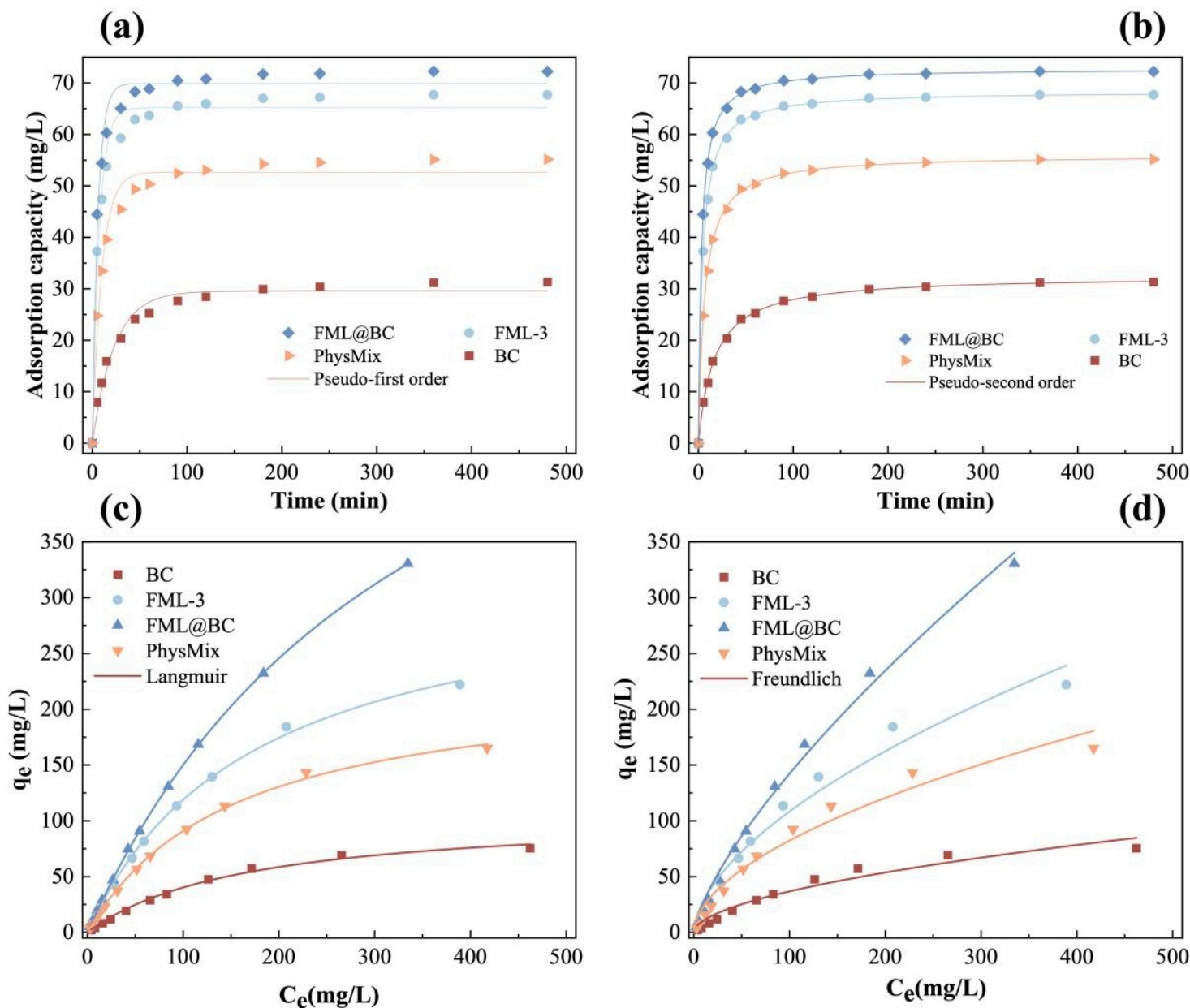


Figure 3

(a) Pseudo-first-order kinetic model fitting for BC, FML-3, FML@BC, and PhysMix; (b) Pseudo-second-order kinetic model fitting for BC, FML-3, FML@BC, and PhysMix; (c) Langmuir isotherm model fitting for BC, FML-3, FML@BC, and PhysMix; (d) Freundlich isotherm model fitting for BC, FML-3, FML@BC, and PhysMix.

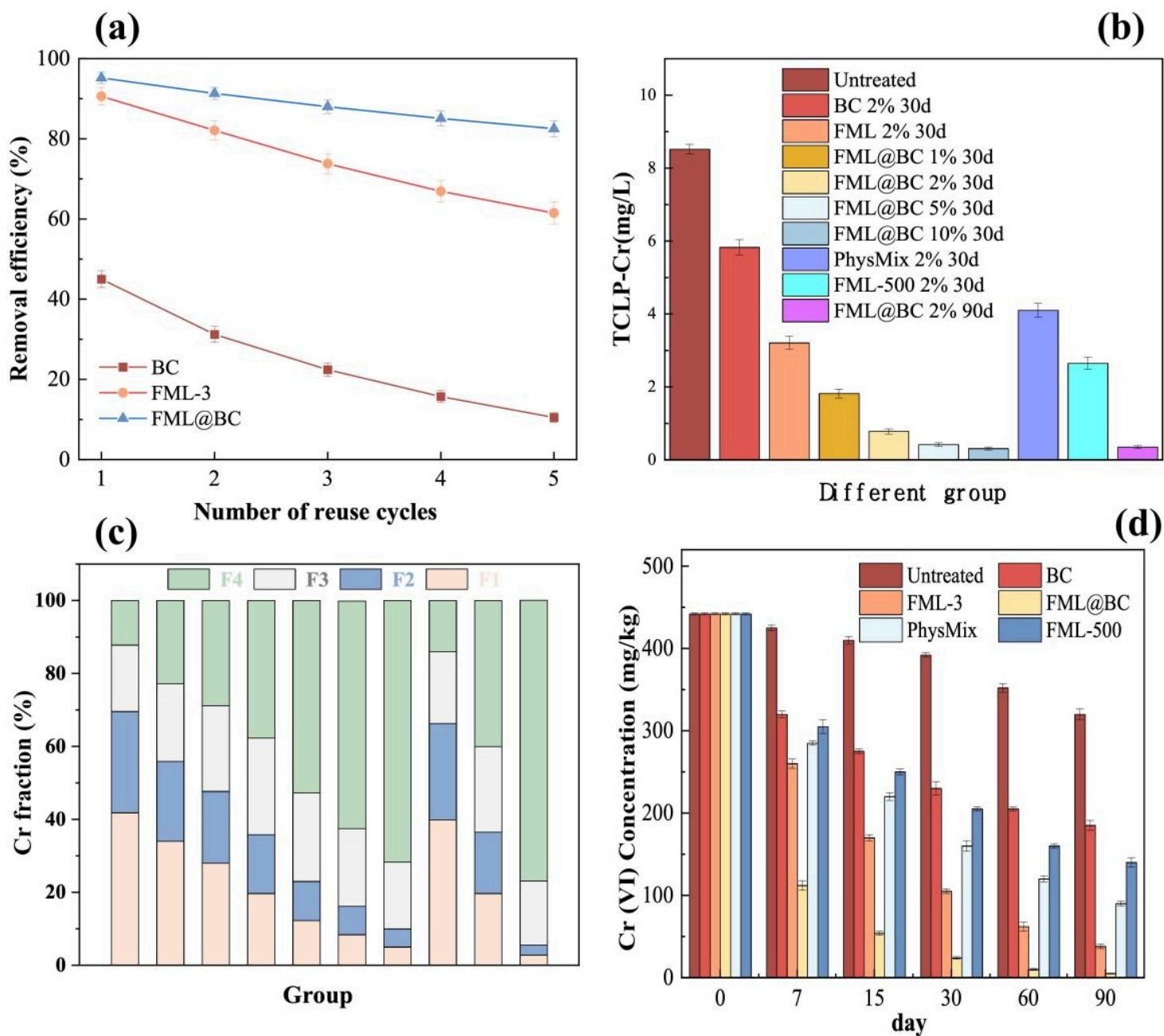


Figure 4

(a) Reusability of BC, FML-3, and FML@BC; (b) TCLP leaching test results of different experimental groups; (c) Chemical speciation distribution of Cr in different experimental groups (F1-F4, with the same x-axis as in (b)); (d) Effect of incubation time on the Cr (VI) immobilization performance of different experimental groups.

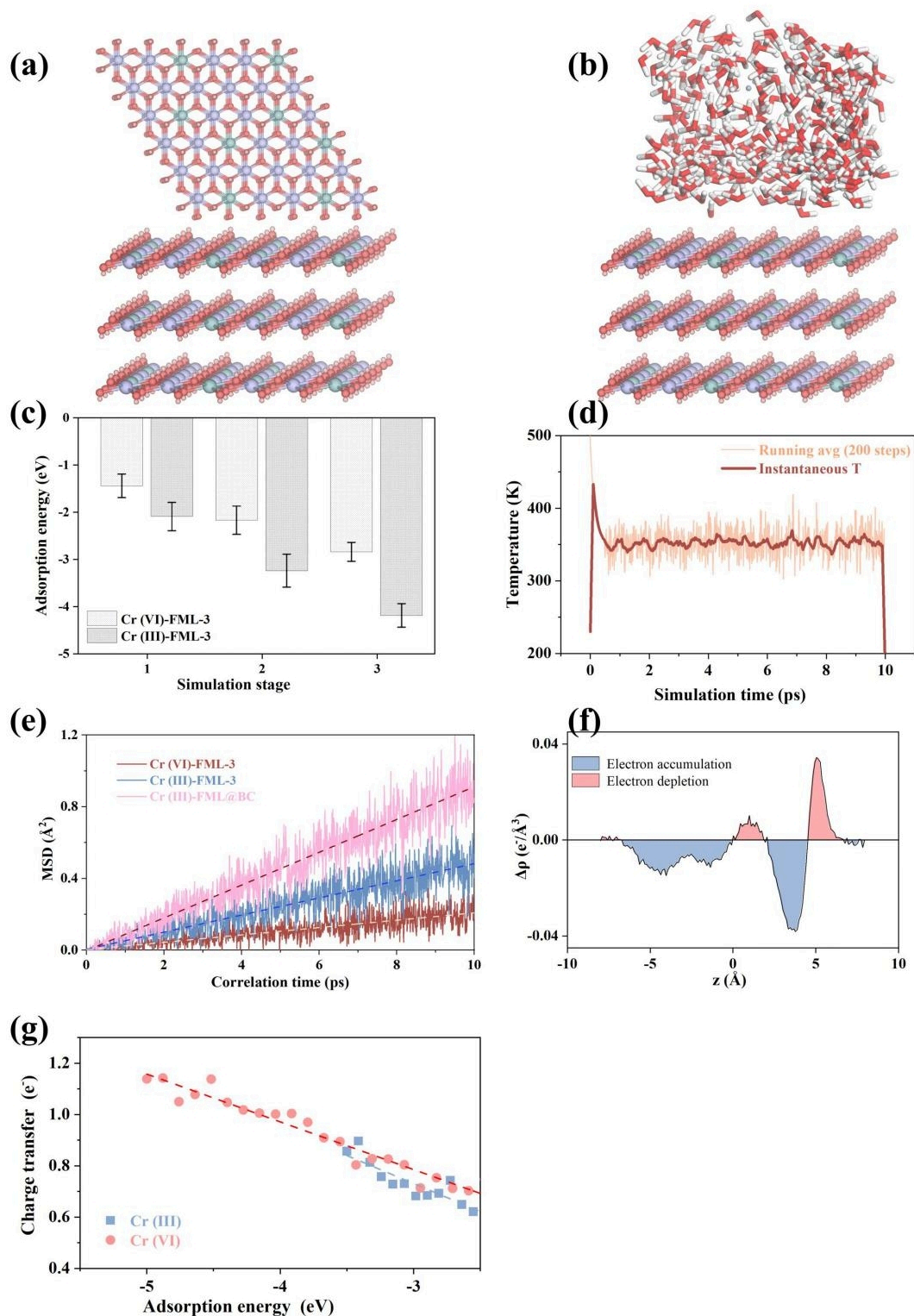


Figure 5

Mechanistic insights from DFT and AIMD simulations. (a) Fe/Mg-LDH (001) slab model. (b) Hydrated interlayer/interface model for AIMD diffusion. (c) Adsorption energies of Cr(VI) and Cr(III) at initial, intermediate, and equilibrium stages. (d) AIMD temperature stability profile. (e) MSD curves and diffusion coefficients (D) for Cr(VI)-LDH, Cr(III)-LDH, and Cr(III)-FML@BC. (f) Charge-density-difference map at the adsorption interface. (g) Net charge transfer for Cr(VI) and Cr(III) on the FML-3 (001) surface.

