

**Zn-H₄dbp/GO for Adsorptive Removal and Zn-H₄dbp/Au for
Electrochemical Reduction of Toxic Cr(VI) in Aqueous Solutions**

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Abstract

In this study, a Zn-based metal-organic framework (MOF) composite, Zn-H₄dbp/GO-5, was engineered by integrating 5 wt% graphene oxide (GO) with Zn-H₄dbp for the efficient adsorption and electrochemical detection of Cr(VI) in aqueous environments. The composite was synthesized via a hydrothermal method using 4,4'-dimethylenebiphenyl diphosphonic acid (H₄dbp), Zn²⁺, and GO, achieving an exceptional Cr(VI) adsorption capacity of 311.8 mg g⁻¹, which surpasses that of comparable materials. The adsorption mechanism followed the Freundlich isotherm and pseudo-second-order kinetic models, revealing multilayer chemisorption dominated by electrostatic interactions between the adsorbent and adsorbate. The composite material maintained over 80% removal efficiency after five adsorption-desorption cycles, benefiting from deprotonated GO-enhanced hydrophobicity. Electrochemically, while Zn-H₄dbp/Au showed superior Cr(VI) detection performance with enhanced reduction peak intensity, sensitivity (2.97 $\mu\text{A mg}^{-1} \text{L cm}^{-2}$), and current density (j) ($j_{\text{aver.}} -4.52 \times 10^{-4} \text{ A cm}^{-2}$), the insulating properties of GO limited the electrochemical response of Zn-H₄dbp/GO composites. The Zn-H₄dbp/Au sensor achieved a detection limit of 2.03 mg L⁻¹ with a linear range of 2–100 mg L⁻¹. These findings highlight Zn-H₄dbp/GO-5 as an outstanding adsorbent for Cr(VI) removal and Zn-H₄dbp/Au as a promising electrochemical sensor, positioning both materials as viable solutions for industrial wastewater treatment.

Keywords

Cr(VI) chemisorption; Metal-organic framework; Graphene oxide; Composite adsorbent; Pseudo-second-order sorption; Moisture endurance, Electrochemical sensor.

1. Introduction

Industrial activities like mining, electroplating, and textile dyeing discharge hexavalent chromium (Cr(VI)), a highly toxic and carcinogenic pollutant, into aquatic environments [1]. Due to its mobility, inertness, and severe health risks, the development of effective Cr(VI) detection and removal methods is critical for safeguarding water quality. Several treatment techniques have been employed, including photocatalytic degradation [2,3], separation-based methods [4], fluorescence spectrometry [5], and adsorption or reduction processes [6]. For instance, a CuO/BCN/MXene dual Z-scheme photocatalyst was developed for visible-light-driven degradation of pollutants [7].

Separation-based techniques also provide accurate detection and quantification. Cathum et al. developed a high-performance liquid chromatography method with diode array detection (HPLC–DAD) using ammonium pyrrolidinedithiocarbamate to determine Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ in environmental samples, with detection limits of 0.007 mg L^{-1} (Cr^{3+}) and 0.004 mg L^{-1} ($\text{Cr}_2\text{O}_7^{2-}$), with high recovery rates [8]. Similarly, reversed-phase HPLC enabled chromium speciation within 10 minutes [9].

Among remediation techniques, adsorption and reduction are particularly attractive due to their simplicity, low cost, and minimal sludge generation [10,11]. Conventional adsorbents such as biomass, zeolites, and carbon-based materials have shown promising results [12]. For instance, Sheikhi et al. developed a lignocellulose biomass nanofiber adsorbent with a Cr(VI) uptake capacity of 344.83 mg g^{-1} [13], while, hexadecyltrimethylammonium functionalized zeolite demonstrated adsorption capacity of 9.83 mg g^{-1} [14]. However, carbon-based adsorbents like graphene suffer from drawbacks such as selectivity, hydrophobicity and aggregation, limiting their effectiveness [15].

To overcome selectivity issues, tailored adsorbents have been introduced. A polystyrene-divinylbenzene resin modified with 2-naphthol-3,6-disulfonic acid successfully separated Cr(III) and Cr(VI) at different pH levels, proving useful for speciation in complex samples [16]. Hybrid methods combining adsorption and optical detection have also advanced. Hettipathirana et al. employed a thin-layer X-ray fluorescence spectrometry (XRFS) method using hydrous ferric oxide for selective Cr(III) adsorption, achieving detection limits down to $1.0 \times 10^{-4} \text{ mg L}^{-1}$ [5]. Likewise, gallic acid-capped gold nanoparticles enabled colorimetric

detection of Cr(III) and Cr(VI) with UV–vis detection limits as low as 0.0026–0.0052 mg L⁻¹ [17].

Despite these advances, conventional adsorbents face notable limitations, such as limited selectivity, poor regeneration, reduced activity in acidic conditions, low electrical conductivity, and finite adsorption capacity including [18]. To address these limitations, researchers are exploring next-generation materials with tailored functionality.

Metal-organic frameworks (MOFs), composed of metal clusters and organic linkers, offer high porosity, tunable structures, and diverse functionalization opportunities [19]. Widely used in catalysis, sensing, and gas storage, MOFs also show promise in heavy metal remediation [20]. However, many MOFs degrade in water or acidic media, compromising long-term use [21]. Functionalization via ligands or post-synthetic modification can improve adsorption efficiency and stability [22].

According to Pearson’s hard-soft acid-base theory, functional groups such as amino (–NH₂), thiols (–SH), and phosphonates (–PO₃²⁻) effectively sequester metal ions [23]. Consequently, amino- and thiol-functionalized MOFs have gained attention for Cr(VI) remediation [24]. For example, Jia et al. developed an amino-functionalized Material of the Institut Lavoisier (MIL), NH₂-MIL-101(Fe), which removed up to 375.20 mg g⁻¹ [25]. Another MOF, NU-56, featuring NH₂-functionalized linkers and Zr₆O₈ nodes, removed Cr(VI) at acidic pH through synergistic Cl⁻ and amine interactions [26]. Meanwhile, SH-functionalized 1,3,5-benzenetricarboxylic acid (BTC)-MOF showed a lower but significant capacity of 15.17 mg g⁻¹ for Cr(VI) [27], and SH-modified Zr-MOFs reached 202 mg g⁻¹, also immobilizing Cr(III) via Cr–thiolate bonding [28].

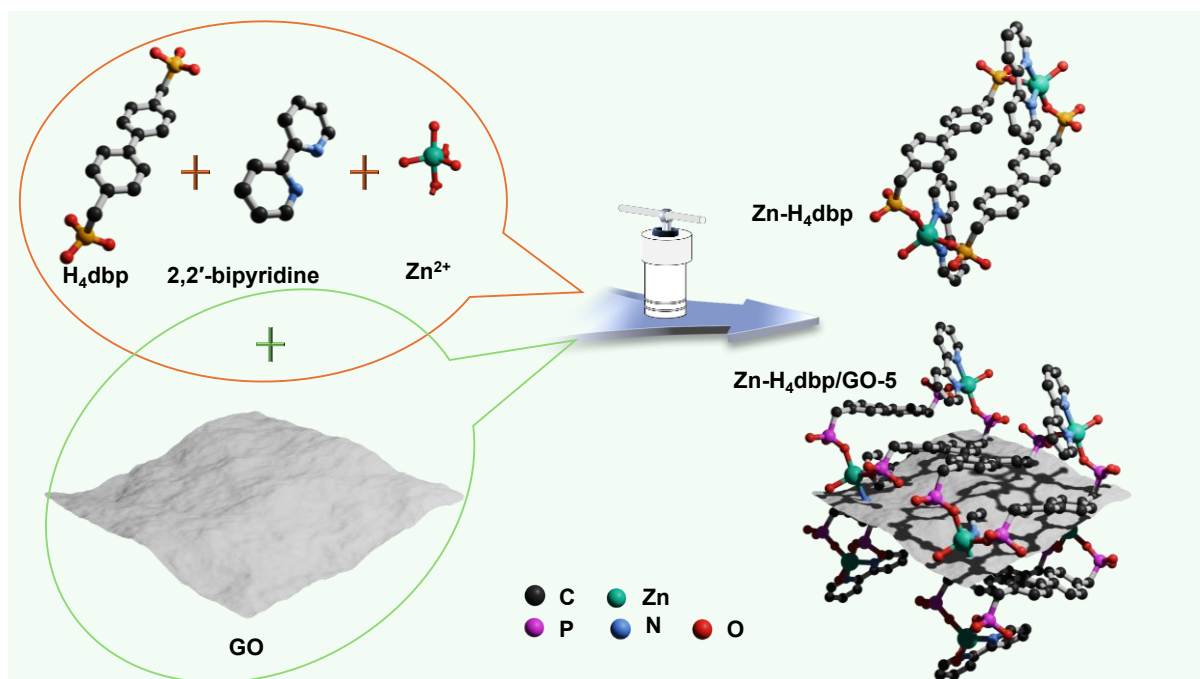
Thiol- and amine-functionalized MOFs have also been widely explored for electrochemical sensing due to their ability to coordinate with metal ions and enhance sensor performance. For instance, MIL-88B(Fe)-NH₂-modified glassy carbon electrode enabled sensitive detection of Cd²⁺, Pb²⁺, and Cu²⁺ [29]. Similarly, Huo et al. employed 3DGO/UiO-66-NH₂ to simultaneously detect multiple metal ions (Cd²⁺, Pb²⁺, Cu²⁺, Hg²⁺) in food samples within three minutes [30]. Likewise, SH-functionalized MIL-100(Fe) demonstrated improved Hg²⁺ extraction (96%) compared to the unmodified form (78%) [31]. Moreover, El-Shishtawy et al. developed a Schiff base-modified electrode that selectively detected Cr³⁺ with a limit of

6.76 × 10⁻⁷ mg L⁻¹ [32]. In a related study, Cr(VI) quantification was also achieved via atomic absorption spectroscopy after electrochemical reduction and Cr(III) preconcentration [33].

However, many thiol- and amine-based MOFs are prone to degradation in acidic or high-ionic-strength environments, limiting their long-term applicability [31,34]. In this context, phosphonate-based MOFs have gained attention due to their superior chemical robustness and coordination capability. Recent studies have shown that phosphonate-MOFs exhibit excellent electrochemical sensing performance for Cr(VI) even in acidic media, offering a promising pathway for stable and selective detection [35,36]. Their characteristic functional groups — P=O, P—OH, and P—O—C not only offer strong anchoring sites on MOF surfaces [37], but also enable robust tridentate coordination, allowing phosphonate linkers to form stable, multidentate bonds with metal ions [38]. This structural feature contributes to the creation of highly porous frameworks with abundant and accessible hydroxyl sites, which significantly improve both the adsorption capacity and electrochemical responsiveness of the material [39]. Furthermore, the inherent reactivity of phosphonate ligands facilitates direct one-step synthesis of MOFs, bypassing the need for post-synthetic modifications and thus improving scalability and reproducibility [40]. Despite these advantages, studies on phosphonate-based MOFs for Cr(VI) removal and sensing remain limited, presenting opportunities for further exploration.

This study introduces one-pot in situ hydrothermal strategy for fabricating Zn-based metal-organic framework (Zn-H₄dbp) integrated with graphene oxide (GO), forming the Zn-H₄dbp/GO composite ([C₂₄H₂₂ZnN₂O₆P₂]_n/GO) (Scheme 1), tailored for efficient Cr(VI) adsorption and electrochemical sensing in aqueous systems. The composite is constructed by combining Zn²⁺ metal centers, the phosphonate-containing linker 4,4'-dimethylenediphenyl diphosphonic acid (H₄dbp), and GO, resulting in improved structural integrity and adsorption capacity. The unsaturated phosphonate groups provide effective Cr(VI) coordination sites, while GO enhances material dispersibility, minimizes aggregation, and optimizes morphological characteristics. The primary goals of this study are to clarify the role of phosphonate groups in Cr(VI) uptake, analyze the adsorption kinetics and isotherms, examine GO's stabilizing effects on performance, and assess the electrochemical detection capabilities of a Zn-H₄dbp-modified Au electrode via square wave voltammetry (SWV). This multifunctional hybrid material offers a promising platform for environmental remediation and heavy metal sensing.

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147 **Scheme 1.** Hydrothermal synthesis and schematic representation of Zn-H₄dbp/GO-5.

148 2. Experimental

149 2.1.1. Preparation of MOF/GO composites

150 The fabrication procedures for GO and H₄dbp are outlined in the supplementary materials.
 151 A mixture of ZnC₄H₆O₄·2H₂O (0.067 g, 0.305 mmol), H₄dbp (0.08 g, 0.234 mmol), 2,2'-
 152 bipyridine (0.03 g, 0.192 mmol), and H₂O (15 g, 0.833 mol) was ultrasonicated for 40 minutes
 153 and heated in a 25 ml Teflon-lined autoclave at 180 °C for 72 hours. After cooling, the white
 154 crystal product, Zn-H₄dbp, was collected and washed with water and acetone. For the
 155 composites, 1, 5, 10, and 15 wt% GO (relative to the core metal) were added to the solution
 156 before hydrothermal treatment, yielding Zn-H₄dbp/GO-1, Zn-H₄dbp/GO-5, Zn-H₄dbp/GO-10,
 157 and Zn-H₄dbp/GO-15, respectively. As GO concentration increased, the solution turned darker.
 158 The resulting products were vacuum filtered, rinsed, and centrifuged for X-ray diffraction
 159 (XRD) analysis.

160 2.1.2. Batch adsorption and regeneration experiments

161 A Cr(VI) stock solution (1000 mg L⁻¹) was prepared by dissolving K₂Cr₂O₇ in deionized
 162 water. The effects of key parameters including adsorbent dosage (0.5–20 mg), solution pH
 163 (2.1–11.9), initial Cr(VI) concentration (2–100 mg L⁻¹), contact time (1–120 min), and

temperature (298–343 K) on Cr(VI) removal efficiency were systematically investigated. The pH was adjusted using NaOH and H₂SO₄, and the adsorbent was dried overnight before the batch adsorption experiments. The influence of ionic strength was assessed by adding NaCl as a background electrolyte. Selective adsorption by Zn-H₄dbp/GO-5 was evaluated in the presence of coexisting ions (NO₃⁻, Ca²⁺, PO₄³⁻, SO₄²⁻, CO₃²⁻, and Al³⁺), each at 0.5 mol L⁻¹, introduced as their respective salts (KNO₃, CaCl₂, Na₃PO₄, K₂SO₄, K₂CO₃, and AlCl₃·6H₂O). Reusability was tested via solvent-driven desorption using a 1:2:1 (v/v/v) mixture of water, methanol, and CH₂Cl₂.

After optimizing the adsorption parameters, the batch adsorption capacity of the adsorbent was examined. At designated time intervals, the supernatant was removed and the residual Cr(VI) was quantified by UV-Vis spectroscopy at 540 nm using 1,5-diphenylcarbazide colorimetric technique [41]. All experiments were performed in triplicate, and average values were considered for data interpretation. The following equations were applied to compute Cr(VI) adsorption performance.

$$q_t = \left(\frac{C_o - C_t}{w}\right) \times V \quad (1)$$

$$\%Removal = \left(\frac{C_o - C_t}{C_o}\right) \times 100, \quad (2)$$

$$Q_e = \left(\frac{C_o - C_e}{w}\right) \times V, \quad (3)$$

where q_t (mg g⁻¹) is the amount of Cr(VI) adsorbed at time t ; C_o (mg L⁻¹) and C_t (mg L⁻¹) are the initial concentration of Cr(VI) and that at time t , respectively; and V (L) and w (g) are the volume of the working aqueous solution and the mass of the adsorbent, respectively; Q_e (mg g⁻¹) is equilibrium adsorption of Cr(VI).

Details of the equilibrium adsorption isotherm, adsorption kinetics and thermodynamic parameters are available in the supplementary materials.

2.1.3. Electrochemical detection of Cr(VI)

The electrochemical detection performance of Zn-H₄dbp and Zn-H₄dbp/GO probes for Cr(VI) was assessed using square wave voltammetry (SWV). The working electrode was prepared by drop-casting 2.0 μL of the MOF dispersed in Nafion/EtOH (20/80 wt.%) onto a gold (Au) electrode, followed by drying at 50 °C. Cyclic voltammetry (CV) was first employed

to determine the redox potential window before conducting SWV measurements using an SP-200 potentiostat with a three-electrode system consisting of an Ag/AgCl (3.0 M KCl) reference electrode, a platinum counter electrode (Φ 0.5 mm $\times$ 50 mm), and a MOF-coated Au working electrode (Φ 3 mm $\times$ 55 mm). SWV was performed at optimized parameters (25 mV amplitude, 50 ms pulse width, -10 mV step potential, 10 s preconcentration) in Cr(VI) solutions (2–100 mg L⁻¹) at pH 4. The influence of common interfering ions (NO₃⁻, Ca²⁺, PO₄³⁻, CO₃²⁻, and Al³⁺) was evaluated by introducing 0.5 mol L⁻¹ of their respective salts to a 10 mg L⁻¹ Cr(VI) solution. All measurements were performed in triplicate, and the sensor's analytical capability was evaluated based on sensitivity, current response, and limit of detection (LOD).

3. Results and discussion

3.1.Characterization

3.1.1. Structural and surface characterization

The purity and properties of the H₄dbp organic linker were verified through nuclear magnetic resonance (NMR) analysis, utilizing both ¹H NMR and ³¹P NMR techniques (**Fig. S1a—c**). X-ray diffraction (XRD) analysis of H₄dbp revealed peaks at $2\theta = 11.83^\circ$, 16.42° , and 22.53° (**Fig. S1d**). In Zn-H₄dbp, the peaks at 11.83° and 16.42° shifted to 12.10° and 16.62° , respectively, while the peak at 22.53° remained unchanged. A new peak appeared at 8.59° , confirming the coordination of Zn²⁺ with H₄dbp. The diffraction pattern of Zn-H₄dbp matched a triclinic crystal structure (P-1 space group) with lattice constants $a = 10.959$ Å, $b = 11.028$ Å, and $c = 11.353$ Å [42]. Key peaks for Zn-H₄dbp appeared at $2\theta = 8.63^\circ$ (001), 11.18° (100), 12.10° (111), 17.08° (101), 22.31° (222), 23.06° (112) and others, aligning with specific crystal planes (**Fig. 1a**). The (001) diffraction peak of pristine GO at $2\theta = 12.18^\circ$ shifted to 13° in the Zn-H₄dbp/GO-5 composite, attributable to reduced interlayer spacing from water molecule removal and partial elimination of oxygenated functional groups, confirming the successful *in situ* incorporation of GO within the composite framework [43].

Fourier transform-infrared spectroscopy (FT-IR) was used to analyze the functional groups in H₄dbp, Zn-H₄dbp, GO, and Zn-H₄dbp/GO-5 (**Fig. 1b**). In H₄dbp, C—H stretching appeared at 3041 cm⁻¹ and 2967 cm⁻¹ [44], with a P—OH group at 2721–1988 cm⁻¹ and P=O at 1666.05

222 cm^{-1} [45]. In Zn-H₄dbp, these features remained, but the P—OH peak decreased, indicating
223 Zn²⁺ integration. Additional peaks at 1170.03, 1091.10, and 829.08 cm^{-1} were attributed to
224 C=N, C—N, and P—O—Zn [46,47]. GO exhibited peaks for O—H stretching (3500–3000
225 cm^{-1}) and 1731.21, 1614.10, 1371.51, 1220.42, 1055.07, and 951.44 cm^{-1} were ascribed to the
226 stretching vibration of C=O, C=C, C—OH [48], C—O—C, C—O, and bending —OH
227 functional groups, respectively [49]. In Zn-H₄dbp/GO-5, a new peak at 1027.9 cm^{-1} confirmed
228 the C—O—Zn bond, and the broad O—H peak at 3410.28 cm^{-1} indicated successful composite
229 formation [50].

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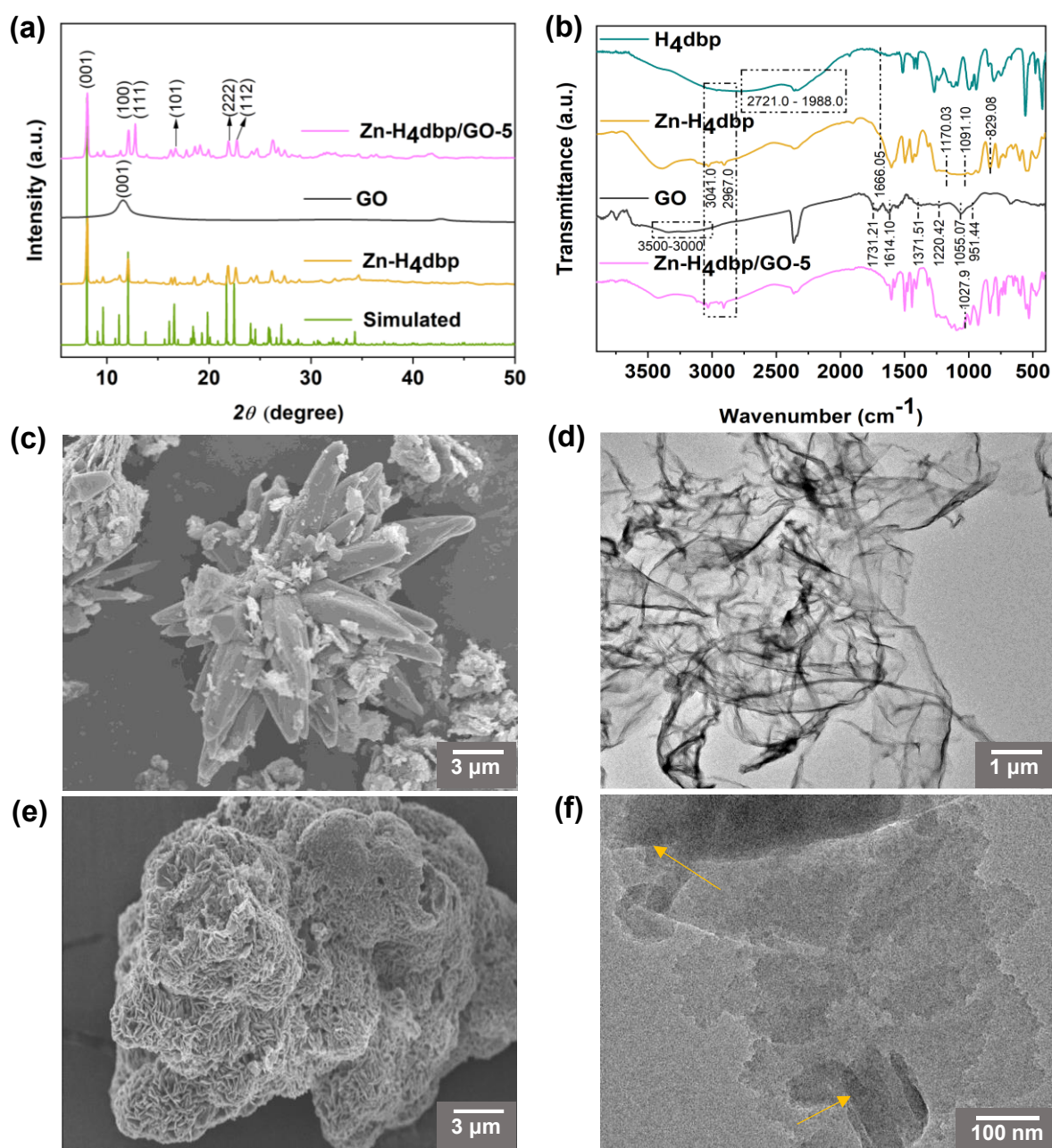


Fig. 1. (a) XRD patterns; (b) FT-IR spectra; FE-SEM images of (c) Zn-H₄dbp, (d) GO, (e) Zn-H₄dbp/GO-5; TEM image of (f) Zn-H₄dbp/GO-5.

The N₂ adsorption-desorption analysis of Zn-H₄dbp and Zn-H₄dbp/GO-5 exhibits hybrid type-I/IV characteristics (**Fig. S1 e**) [51], featuring both a sharp uptake at low P/P_0 (<0.1), indicative of microporosity, and a distinct hysteresis loop at higher P/P_0 (>0.4), confirming mesoporosity. This combined behavior demonstrates their hierarchical porous structure [52].

The Brunner-Emmett-Teller (BET) analysis reveals similarly low surface areas (20.03 m² g⁻¹ for Zn-H₄dbp and 20.09 m² g⁻¹ for Zn-H₄dbp/GO-5), suggesting that GO incorporation has negligible impact on surface area. This observation is attributed to the dense framework formed by the phosphonic acid-based H₄dbp linker. Barrett-Joyner-Halenda (BJH) pore-size distribution analysis, however, highlights structural differences: Zn-H₄dbp displays a hierarchical pore structure with meso- and macropores (20–40 nm range and a peak at ~550 nm), whereas Zn-H₄dbp/GO-5 exhibits a narrower mesoporous distribution (centered at 3–5 nm) along with reduced pore volume and diameter [53].

While BET-derived isotherm reflects contributions from both micro- and mesoporosity, BJH emphasizes mesoporous features due to its limited sensitivity to micropores, highlighting the need for complementary methods such as t-plot or DFT [54]. Despite negligible changes in surface area, GO integration enhances pore uniformity and structural stability [55]. The hierarchical porosity of Zn-H₄dbp/GO-5, which combines the high adsorption capacity of micropores with the accessibility of mesopores for diffusion, makes it highly effective for removing heavy metals from water [56].

The thermal stability of the as-fabricated materials was investigated using thermogravimetric analysis (TGA) pyrogram and derivative thermogravimetric analysis (DTGA), covering a range of 28 to 800 °C (at 10 °C/min) (**Fig. S1 f**). For Zn-H₄dbp, an initial 4.0% weight loss between 28–150.04 °C was attributed to moisture loss and hydroxyl condensation [57], supported by exothermic DTGA peaks at 72.74 °C and 106.84 °C [58]. Major decomposition events at 291.08 °C and 501.52 °C were assigned to the breakdown of phosphonic acid and bipyridine ligands, respectively, leading to a total mass loss of ~31.0% [59]. A strong DTGA peak at 311.94 °C correlated with phosphonic acid degradation, while peaks at 352.36 °C and 397.28 °C indicated further organic breakdown [60]. The 537.51 °C peak (corrected from 537.509 for consistency) reflected bipyridine decomposition. Negative DTGA peaks at 90.71 °C and 568.11 °C suggested endothermic moisture loss and phase transformation into stable inorganic phases such as ZnO or zinc phosphate [61].

GO showed an 18.70% weight loss between 28 °C and 175.94 °C, primarily due to the release of adsorbed moisture [58]. A major mass loss of 19.20% occurred between 191.52 °C and 280.21 °C, assigned to the decomposition of labile oxygen-containing groups (e.g., epoxy, carboxyl, and hydroxyl) [50]. This observation is supported by a single DTGA peak at

217.46 °C, indicating a dominant degradation event. Above 286.93 °C, a gradual weight loss persisted up to 800 °C, associated with the removal of more stable oxygen functionalities and progressive carbonization of GO [62]. The final residue is likely composed of disordered or partially graphitized carbon.

The Zn-H₄dbp/GO-5 composite exhibited three distinct degradation steps at 208.77 °C (GO), 401.56 °C (H₄dbp), and 523.50 °C (bipyridine), indicating altered thermal properties from component interactions [63,64]. These were corroborated by DTGA peaks at 223.78 °C, 461.15 °C, and 569.78 °C, corresponding to exothermic decomposition of the respective components [65]. A minor exothermic peak at 106.01 °C was attributed to adsorbed moisture loss. The sharp, well-resolved DTGA peaks demonstrate distinct and staged decomposition processes. Above 579.97 °C, a gradual weight loss persisted up to 800 °C, resulting from residual organic breakdown and formation of a stable inorganic phase (e.g., ZnO or Zn₃(PO₄)₂) [66]. The composite's enhanced thermal stability suggests its applicability for heavy metal adsorption under ambient wastewater conditions.

Water contact angle measurements were performed under ambient conditions (using Young's equation) to evaluate the moisture interaction properties of Zn-H₄dbp/GO-5 and its constituent materials [67]. All samples were dried and prepared as uniform films before analysis. The H₄dbp ligand, rich in hydrophilic –OH groups, exhibited complete wetting behavior (0° contact angle, **Fig. S2a**). In contrast, pristine GO showed intermediate hydrophilicity (29.3°, **Fig. S2b**), while Zn-H₄dbp demonstrated reduced wettability (41.8°, **Fig. S2c**) due to –OH deprotonation during Zn²⁺ coordination. The Zn-H₄dbp/GO-5 composite displayed significantly enhanced hydrophobicity (56.0°, **Fig. S2d**) [68], resulting from further –OH deprotonation during composite formation. Additionally, deprotonated GO serves as a rigid, hydrophobic scaffold that stabilizes the Zn-H₄dbp structure and improves dispersion in solutions [69], contributing to the composite's superior heavy metal adsorption performance in aqueous environments.

3.1.2. Morphology and elemental composition

Fig. 1 presents the field emission-scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) characterization of Zn-H₄dbp/GO-5 and its individual components. The pristine Zn-H₄dbp exhibits a well-defined ellipsoid-rod morphology arranged in a flower-like cluster (**Fig. 1c**). The GO exhibit a wrinkled, sheet-like structure with a gray, undulated surface, characteristic of its organic layers (**Fig. 1d**). In contrast, the Zn-H₄dbp/GO-5 composite shows an irregular, wrinkled crystalline structure that aggregates into larger domains (**Fig. 1e**). TEM analysis of the composite (**Fig. 1f**) reveals scattered dark patches on a gray organic matrix, with dark inorganic dots corresponding to the Zn²⁺ ions, indicating successful incorporation of Zn-H₄dbp and GO into a unique composite material.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemistry of the materials. The H₄dbp organic linker shows P 2p peaks at 133.25 eV (C—P), 134.33 eV (P—OH), 134.91 eV (P=O); C 1s peaks at 284.29 eV (C=C), 284.35 eV (C—C), 285.63 eV (C—P); and O 1s peaks at 531.28 eV (P—OH) and 532.76 eV (P=O), consistent with expected bonding energies (**Fig. S3b—d**) [70,71]. **Fig. S3e—f** shows XPS analysis of graphene oxide (GO), with the C 1s spectrum shows peaks at 284.10 eV (C=C/C—C), 284.75 eV (C=C), 285.74 eV (C—C), 286.71 eV (C—OH/C—O—C), 287.51 eV (C=O), and 288.89 eV (O—C=O) [72]. The oxygen functional groups at 532.49 eV (C=O, C—O), 531.82 eV (C—OH), 532.93 eV (O—C=O), and 533.68 eV (OH, adsorbed water), confirming the diverse oxidation states and functional groups present in GO.

Distinct shifts in binding energies between pristine Zn-H₄dbp and the Zn-H₄dbp/GO-5 composite reveal chemical interactions of Zn-H₄dbp with GO (**Fig. 2a**). In pristine Zn-H₄dbp, the P 2p peaks appear at 133.37 eV (P=O) and 132.89 eV (P—O/P—O—Zn). Upon composite formation, these peaks shift to 133.74 eV (+0.37 eV) and 132.46 eV (−0.43 eV), respectively (**Fig. 2b**) [73–75]. Additionally, a new peak emerges at 133.50 eV, attributed to P—OH, likely due to uncoordinated ligands and hydroxyl groups from GO. These changes indicate enhanced coordination and chemical modification in the composite.

In the Zn-H₄dbp, the C 1s XPS peaks at 284.53, 285.00, 286.27, and 286.70 eV corresponding to sp² C—C/C=C, C—P, C—N/C=N, and minor oxygen-associated carbon groups, respectively (**Fig. 2c**) [76]. Upon forming the Zn-H₄dbp/GO-5 composite, these peaks

shift to 284.77, 285.72, 286.22, and 286.77 eV [77]. The C—C/C=C peak at 284.77 eV shifts by +0.24 eV, indicating electronic interaction with GO. A more pronounced shift of +0.72 eV for the C—P (285.72 eV), demonstrating strong charge redistribution and enhanced chemical bonding with GO [78]. Meanwhile, the C—N/C=N peak shifts from 286.27 eV in the Zn-H₄dbp to 286.22 eV in the composite (−0.05 eV), suggesting slight electronic adjustments. Additionally, the emergence of epoxy (C—O) groups at 286.22 eV and the shift of the carboxyl (COOH) peak from 286.70 to 286.77 eV (+0.07 eV) highlight the chemical contributions of GO. These binding energy changes, coupled with the appearance of additional functional groups, confirm the successful integration of GO, and collectively alter the electronic environment while increasing the composite's chemical complexity.

The N 1s XPS spectrum of Zn-H₄dbp shows peaks at ~399.89 eV (C—N/C=N) and ~400.09 eV (N—Zn), which reflect the bonding environment of 2,2-bipyridine and its coordination to zinc (**Fig. 2d**) [79]. In the Zn-H₄dbp/GO-5 composite, the C—N/C=N peaks shift to ~399.80 eV (a −0.09 eV change), indicating GO-induced electronic modulation. Conversely, the N—Zn peaks undergoes a significant +2.22 eV shift to ~402.31 eV, attributed to stronger N—Zn---O interactions with GO's oxygen functionalities. These shifts demonstrate GO's influence on the composite's coordination chemistry.

The O 1s spectrum of Zn-H₄dbp displays peaks at 531.33 eV (P—OH), 531.92 eV (P—O—Zn), and 533.00 eV (P=O) (**Fig. 2e**) [80]. In the Zn-H₄dbp/GO-5 composite, the P—OH peak shifts slightly to 531.24 eV (−0.09 eV), and the P—O—Zn peak shifts to 531.90 eV (−0.02 eV), suggesting weak coupling due to interactions with GO [81]. The P=O peak remains unchanged at 533.00 eV, demonstrating its stability, while new peaks at 532.91 eV (OH) and 533.72 eV (C—O—C/COOH) emerge, originating from GO's, reflecting the influence of GO on the bonding environment in the composite.

The Zn 2p spectrum of Zn-H₄dbp exhibits doublet peaks at 1022.25 eV and 1022.33 eV for Zn—O and Zn—N bonds, respectively, with corresponding Zn 2p_{1/2} peaks at 1045.32 eV and 1045.45 eV (**Fig. 2f**) [82,83]. The Zn—N bond is attributed to crosslinking with the 2,2-bipyridine ligand. In the Zn-H₄dbp/GO-5, the Zn 2p_{3/2} peaks shift to 1022.42 eV (+0.17 eV) and 1022.61 eV (+0.28 eV), while the Zn 2p_{1/2} peaks shift to 1045.63 eV (+0.31 eV) and 1045.70 eV (+0.25 eV). These shifts suggest modifications in both the Zn—O and Zn—N bonding environments, with Zn—O experiences a larger shift, implying stronger interactions

between Zn^{2+} and both the organic linker and GO.

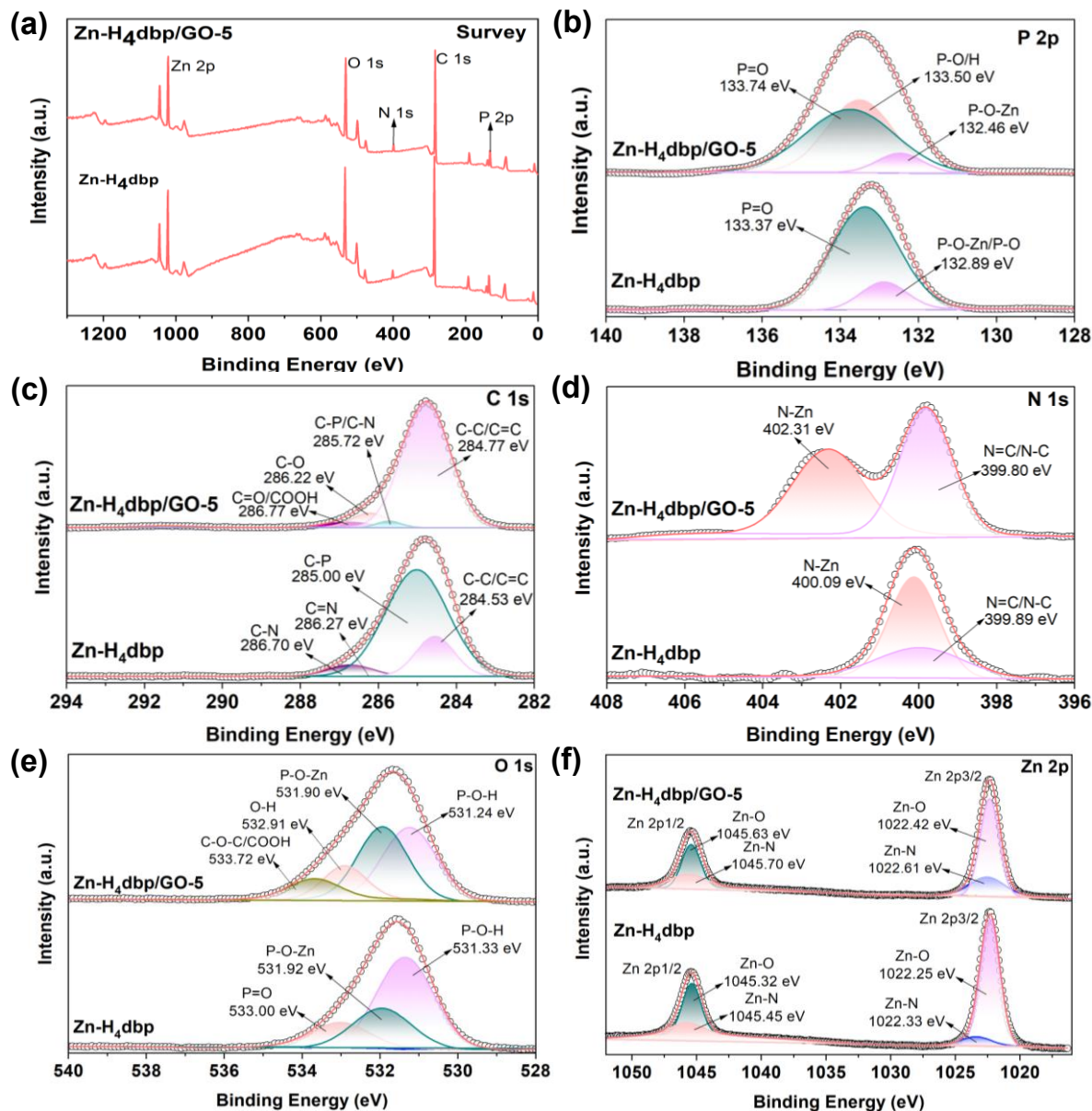


Fig. 2. XPS spectra of Zn-H₄dbp and Zn-H₄dbp/GO-5: (a) survey, (b) P 2p, (c) C 1s, (d) N 1s, (e) O 1s, and (f) Zn 2p spectra.

3.2.Cr(VI) Batch Adsorption

The adsorption capacity of Zn-H₄dbp/GO-5 for Cr(VI) sharply increased from 60.34 mg

g⁻¹ to 312.02 mg g⁻¹ as Cr(VI) concentration elevated from 20 mg L⁻¹ to 100 mg L⁻¹ (**Fig. S4a**). Notably, Zn-H₄dbp/GO-5 with 5 wt% GO exhibited the best performance. Higher GO concentrations induced to agglomeration, thereby reducing accessible sites, while lower concentrations maintained favorable interlayer distance and surface area (**Fig. S4b—d**) [84]. Thus, 5 wt% GO was optimal loading for maximizing Cr(VI) adsorption. Compared to its individual components, Zn-H₄dbp/GO-5 demonstrated significantly improved adsorption capacity, highlighting the synergistic effects of the composite (**Fig. S5a—d**). Specifically, GO not only protects the metal cluster but also provides abundant hydroxide groups for binding, while Zn-H₄dbp contributes its high-density active sites. Furthermore, the effects of key parameters, including adsorbent dosage, pH, initial concentration, and contact time on adsorption performance, were systematically studied.

3.2.1. Effect of adsorbent amount

The optimal Zn-H₄dbp/GO-5 dosage for Cr(VI) removal was determined to be 15 mg for a 50 mL solution, effective across all tested concentrations (**Fig. 3a**). This dosage was used for subsequent adsorption kinetic and isotherm studies.

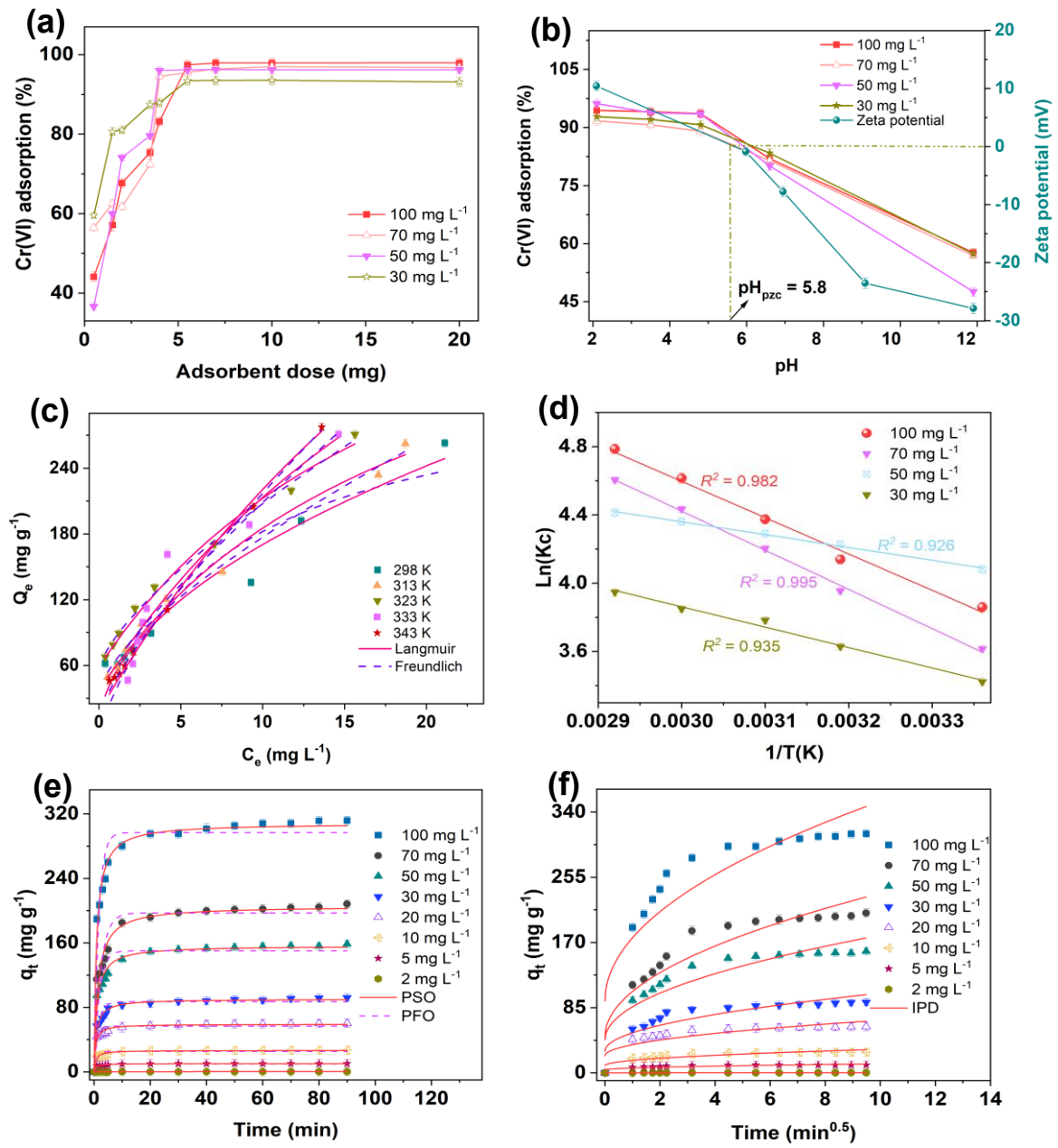


Fig. 3. Experimental results to determine the optimal Cr(VI) adsorption conditions for Zn-H₄dbp/GO-5: (a) adsorbent dosage, (b) the effect of pH on the adsorption capacity and zeta potential, (c) adsorption isotherms at various temperatures, (d) thermodynamic parameters of Cr(VI) adsorption by Zn-H₄dbp/GO-5; (e) Adsorption kinetics of Cr(VI) adsorption by Zn-H₄dbp/GO-5 the PFO and PSO models, and (f) the IPD model.

3.2.2. Effects of solution pH and contact time

Cr(VI) adsorption on Zn-H₄dbp/GO-5 achieved >90% efficiency at pH 2.1–6.6, driven by dominance HCrO₄[−] species in solution and protonated adsorbent surface (**Fig. 3b**) [85]. Above the point of zero charge (pH_{pzc} = 5.8), adsorption declined sharply owing to −OH[−] competition and electrostatic repulsion between anionic Cr(VI) species and negatively charged surfaces. The optimal adsorption pH occurred at 4.0, where kinetic studies revealed 90% removal within 30 minutes, reaching near-equilibrium (~90% removal) at 60 minutes and full equilibrium by 90 minutes.

3.2.3. Adsorption isotherms

The equilibrium adsorption data were analyzed using both Langmuir and Freundlich isotherm models, with parameters determined through non-linear regression. The Langmuir model assumes monolayer adsorption on a finite number of homogeneous active sites, while the Freundlich model describes multilayer adsorption on heterogeneous surface [86]. The Cr(VI) adsorption isotherm of Zn-H₄dbp/GO-5 was analyzed at five temperatures (298 K, 313 K, 323 K, 333 K, 343 K) (**Fig. 3c**). The Freundlich model provided a better fit, with R² values of 0.941 (298 K) and 0.997 (343 K), whereas the Langmuir model showed poorer correlation (**Table 1**). According to Freundlich model, the experimental maximum adsorption capacity reached 311.77 mg g^{−1} for 100 mg L^{−1} Cr(VI), while the Langmuir-fitted value was 326.42 mg g^{−1}. Notably, Zn-H₄dbp exhibited Langmuir model with a maximum capacity of 148.79 mg g^{−1} (**Table S1**), indicating monolayer adsorption (**Fig. S6a**).

The observed discrepancy in adsorption isotherms is primarily stems from fundamental differences in surface characteristics of the materials [87]. While, Zn-H₄dbp exhibit Langmuir model, indicating monolayer adsorption on a homogeneous surface, Zn-H₄dbp/GO-5 demonstrates Freundlich model due to the heterogeneous surface introduced by GO [88]. This heterogeneity arises from oxygen-containing functional groups (e.g., hydroxyl, epoxy, carboxyl) and structural defects in GO, which create energetically diverse adsorption sites with distinct binding affinities [89]. Such surface complexity facilitates multilayer adsorption, accounting for the composite's Freundlich isotherm pattern.

Table 1. Adsorption isotherm parameter values for Cr(VI) adsorption by Zn-H₄dbp/GO-5.

Temperature (K)		298	313	323	333	343
Langmuir	$Q_{m,c}$ (mg g ⁻¹)	326.42	520.35	641.77	970.26	1154.0
	K_L (L mg ⁻¹)	0.126	0.059	0.065	0.044	0.025
	R_L	0.074	0.145	0.133	0.185	0.286
	R^2	0.841	0.987	0.988	0.904	0.993
Freundlich	K_F (mg g ⁻¹)	52.92	35.59	45.52	42.57	33.38
	$1/n$	0.507	0.718	0.745	0.848	0.836
	R^2	0.941	0.991	0.994	0.896	0.997

$Q_{m,c}$, maximum adsorption capacity; K_L , Langmuir isotherm constant; R_L , adsorption favorability constant; K_F , Freundlich isotherm constant; $1/n$, ratio of heterogeneity constant.

3.2.4. Thermodynamic parameters

Zn-H₄dbp demonstrates increased Cr(VI) adsorption at higher temperatures (**Fig. S6b**), with negative ΔG values indicating a spontaneous process. The positive ΔH and ΔS values suggest that the adsorption is endothermic and entropically favored, as higher temperatures improve solubility and promote faster kinetics (**Table S2**). Similarly, the Zn-H₄dbp/GO-5 composite exhibits enhanced Cr(VI) adsorption at elevated temperatures (**Fig. 3d**), with spontaneous adsorption accompanied by greater disorder, as evidenced by the positive ΔH and ΔS values (**Table S3**).

3.2.5. Adsorption kinetics

The Cr(VI) adsorption kinetics were evaluated using the Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), and Webber-Morris' Interparticle Diffusion (IPD) models. The PSO model, indicative of chemisorption, provided a superior fit Zn-H₄dbp/GO-5 than the PFO model, with higher R^2 values (e.g., 0.954 and 0.986 at 2 mg L⁻¹ and 100 mg L⁻¹, respectively, compared to 0.922 and 0.930 for PFO; **Table S4**). The experimental Cr(VI) removal (311.77

mg g⁻¹) closely matched the PSO-predicted value (308.57 mg g⁻¹), further supporting the chemisorption as dominant mechanism (**Fig. 3e**). Moreover, Zn-H₄dbp/GO-5 composite exhibited the highest Cr(VI) uptake capacity, as compared to other materials (**Table S5**). Similarly, the Cr(VI) adsorption kinetics for pristine Zn-H₄dbp were also well-explained by the PSO model (**Fig. S6c**). At 100 mg L⁻¹, Zn-H₄dbp adsorbs 182.47 mg g⁻¹ with R² 0.939 fitting constant (**Table S6**). In contrast, the IPD model showed no linear relationship and was less effective in determining the rate-limiting step for both Zn-H₄dbp and the composite (**Fig. S6d & Fig. 3f**) [90].

3.2.6. Effects of ionic strength and competing ions

The presence of NaCl in the Cr(VI) solution reduces adsorption by weakening electrostatic interactions [91]. At 0.05 mol L⁻¹ NaCl, adsorption decreased by 8.63%, while a higher concentration (1 mol L⁻¹) led to a 40% reduction (**Fig. 4a**). This suppression occurs because NaCl increases the ionic strength, screening the electrostatic attraction between Cr(VI) ions and the adsorbent surface. However, at even higher NaCl concentrations, the effect plateaued, indicating that non-electrostatic mechanisms (e.g., chemical binding or surface complexation) also contribute to adsorption.

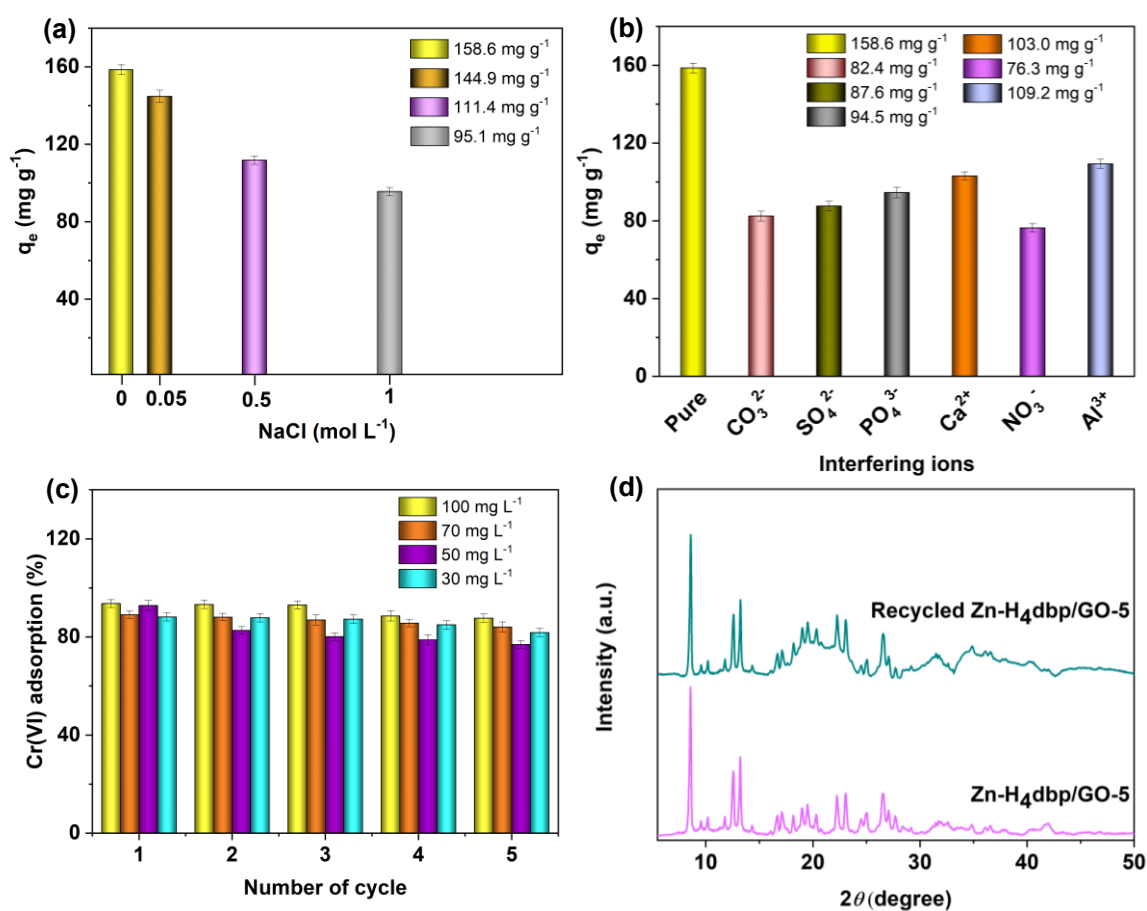


Fig. 4. (a) ionic strength, (b) influence of coexisting ions on Cr(VI) adsorption by Zn-H₄dbp/GO-5; (c) recoverability of Zn-H₄dbp/GO-5 and (d) exhaust adsorbent XRD spectrum.

The influence of coexisting ions (NO_3^- , Ca^{2+} , PO_4^{3-} , SO_4^{2-} , CO_3^{2-} , Al^{3+}) on Cr(VI) adsorption by Zn-H₄dbp/GO-5 was investigated. As shown in **Fig. 4b**, NO_3^- competed with HCrO_4^- for adsorption sites, significantly reducing Cr(VI) uptake [92]. Divalent (Ca^{2+} , SO_4^{2-}) and trivalent (PO_4^{3-} , Al^{3+}) ions had minimal impact, whereas CO_3^{2-} substantially affected adsorption through pH elevation by generating OH^- and subsequent alteration of the Zn-H₄dbp/GO-5 surface charge.

3.2.7. Adsorption mechanism

The adsorption mechanism of Cr(VI) on Zn-H₄dbp/GO-5 involves coordinated chemical interactions that are strongly pH-dependent. The process begins with the coordination

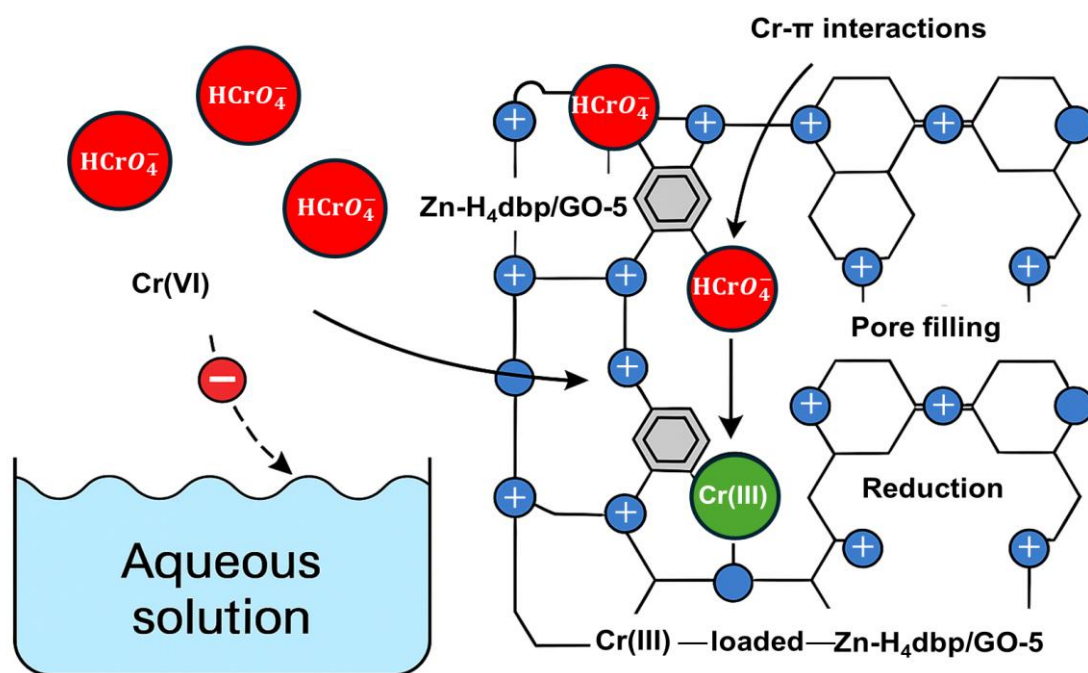
chemistry of the adsorbent: the H₄dbp ligand coordinates with Zn²⁺ via deprotonation of its —OH groups (along with additional —OH from GO), forming H₂dbp²⁻ complexes. At pH 4.0, where the adsorbent surface carries a positive charge (**Scheme 2**), Cr(VI) removal occurs through three consecutive steps: (1) protonation of —OH groups to form —OH₂⁺; (2) electrostatic attraction between cationic adsorbent and anionic Cr(VI) species (HCrO₄⁻); and (3) subsequent reduction of Cr(VI) to Cr(III) mediated by electron-donating —OH groups (Eq. 4).



Cr(III) forms coordinated covalent connections with Zn-H₄dbp/GO-5 through the following mechanism:



XPS analysis across pH 2.1–12.2 revealed this reduction is most efficient under acidic conditions, with Cr(III) fractions of 62.07% (pH 2.1, **Fig. S7b**) and 60.2% (pH 4.0, **Fig. S7c**) decreasing to 41.09% at pH 12.2 (**Fig. S7g**) [93]. As shown in **Fig. S7h**, the pH dependence correlates strongly ($R^2 = 0.896$) with surface charge, where the positive zeta potential at low pH enhances both electrostatic Cr(VI) adsorption and proton-assisted electron transfer. These results confirm that electrostatic interactions critically promote the chemical reduction of Cr(VI). The removal mechanism involves primary chemisorption through coordination-coupled reduction (supported by PSO kinetics), followed by secondary physical interactions including pore filling and cation- π effects [94].



Scheme 2. Adsorptive mechanism of Cr(VI) from aqueous solution by the Zn-H₄dbp/GO-5.

3.2.8. The Zn-H₄dbp/GO-5 stability

Zn-H₄dbp/GO-5 maintained exceptional recyclability, achieving over 87.7% Cr(VI) removal after five cycles (**Fig. 4c**), with its adsorption capacity exceeding 80% for various concentrations. The modest 5.9% reduction in adsorption capacity at 100 mg L⁻¹ Cr(VI) was primarily caused by residual Cr(VI) occupying active sites. XRD characterization of recycled Zn-H₄dbp/GO-5 (**Fig. 4d**), revealed both excellent retention of the framework's primary crystalline structure (evidenced by persistent characteristic diffraction peaks) and partial surface amorphization (manifested as broad scattering features between 17.58° and 25.26° 2θ). This localized structural change likely stems from Cr(VI/III) coordination during adsorption-reduction, yet the overall metal-organic framework remains intact, underscoring the material's operational stability. Complementary FT-IR analysis detected Cr(III)—O bonds formation at 1040.69 cm⁻¹ (**Fig. S8**), confirming —OH groups involvement in Cr(III) complexation. Collectively, these results demonstrate outstanding retention of both structural integrity and chemical functionality throughout repeated adsorption-desorption cycles.

3.3.SWV-based Cr(VI) detection

Cyclic voltammetry (CV) was employed to assess the electrochemical reduction behavior of Cr(VI) on various electrodes [95]. The bare Au electrode exhibited two distinct reduction peaks at 0.132 V and -0.287 V (**Fig. 5a**), consistent with the two-stage reduction of Cr(VI) to Cr(III). By contrast, the Zn-H₄dbp/Au electrode displayed only a single reduction peak at 0.123 V (**Fig. 5b**), suggesting modified reaction pathways. The composite electrodes (Zn-H₄dbp-GO-1/Au and Zn-H₄dbp-GO-5/Au) exhibited broader reduction peaks centered at 0.015 V and -0.043 V, respectively (**Fig. 5c & d**), indicating altered electrochemical kinetics. Comprehensive CV studies across Cr(VI) concentrations (2 – 100 mg L⁻¹) confirmed the optimal potential window of -0.8 V to 0.8 V for sensor characterization (**Fig. S9**). As illustrated in **Scheme S1**, Cr(VI) undergoes reversible redox behavior, with minimal oxidation of Cr(III) back to Cr(VI) due to its inert state.

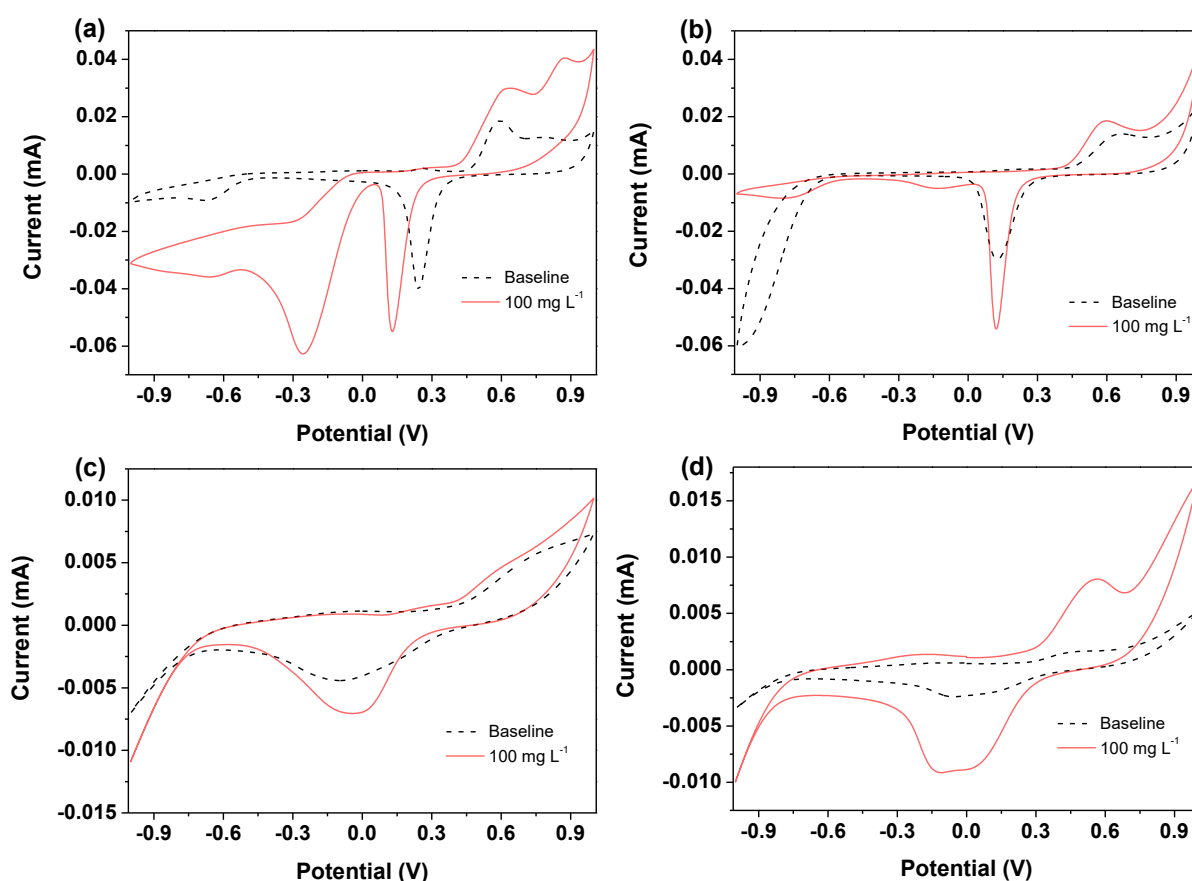


Fig. 5. Cyclic voltammetry (CV) study of the baseline and 100 mg L⁻¹ Cr(VI) working solution: (a) Bare Au electrode, (b) Zn-H₄dbp/Au, (c) Zn-H₄dbp-GO-1/Au, and (d) Zn-H₄dbp-GO-5/Au.

523

524 All electrodes showed distinct SWV reduction peaks for Cr(VI), indicating altered
525 electrochemical behavior upon analyte introduction. The bare Au electrode exhibited multiple
526 reduction peaks in the H₂SO₄ electrolyte at (0.19 V, −0.08 V, and −0.67 V), corresponding to
527 diverse surface processes (**Fig. S10a**) [96]. Following addition of 100 mg L^{−1} Cr(VI) solution,
528 these peaks shifted to 0.062 V, −0.252 V, and −0.665 V, accompanied by increased current
529 intensities, demonstrating strong interactions between Cr(VI) species and the Au surface.
530 Notably, the bare Au electrode's complex multi-peak response, highlighting stepwise Cr(VI)
531 reduction pathways and inherent limitations in catalytic efficiency.

532 In contrast to the bare Au electrode, the Zn-H₄dbp/Au electrode displayed only a single
533 baseline reduction peak at 0.05 V. Upon exposure to 100 mg L^{−1} Cr(VI), however, three distinct
534 peaks appeared at 0.04 V, −0.15 V, and −0.69 V. The most prominent peak at 0.04 V
535 demonstrated sharp intensity, significantly enhancing Cr(VI) detection sensitivity while
536 enabling a more efficient reduction process near zero potential (**Fig. S10b**).

537 The SWV-based detection of Cr(VI) was systematically investigated across
538 concentrations range from 2–100 mg L^{−1}. For the bare Au electrode, reduction peaks shifted to
539 more negative potentials with increasing Cr(VI) concentrations (**Fig. 6a**). The primary peak
540 shifted from 0.178 V to 0.062 V, the secondary peak moved from −0.019 V to −0.257 V, and
541 the tertiary peak (observed near −0.631 V) corresponded to Cr(III) reduction to lower oxidation
542 states [97], confirming a stepwise reduction mechanism. The peak current exhibited a strong
543 linear correlation ($R^2 = 0.998$; inset **Fig. 6a**), yielding an area-normalized sensitivity of 4.52
544 $\mu\text{A mg}^{-1} \text{L cm}^{-2}$.

545 In contrast, the Zn-H₄dbp/Au electrode exhibited a single reduction peak that
546 progressively shifted to a lower potential with increasing Cr(VI) concentrations (**Fig. 6b**),
547 achieving an area-normalized sensitivity of 2.97 $\mu\text{A mg}^{-1} \text{L cm}^{-2}$. This performance surpassed
548 composite electrodes (Zn-H₄dbp/GO-1/Au: 0.99 $\mu\text{A mg}^{-1} \text{L cm}^{-2}$; Zn-H₄dbp/GO-5/Au: 0.28
549 $\mu\text{A mg}^{-1} \text{L cm}^{-2}$; **Fig. 6c & d**). Additionally, the Zn-H₄dbp/Au electrode demonstrated higher
550 current density, increasing from $-2.83 \times 10^{-4} \text{ A cm}^{-2}$ (2 mg L^{−1}) to $-5.77 \times 10^{-4} \text{ A cm}^{-2}$ (100 mg
551 L^{−1}), further highlighting its superior performance. These enhancements stem from the
552 electrode's intrinsic electrocatalytic activity and efficient electron transfer (**Fig. S11**). Limit of
553 detection (LOD, 3 σ /S) analysis reinforced its practicality, with values of 2.028 mg L^{−1} (Zn-

H₄dbp/Au), 6.269 mg L⁻¹ (Zn-H₄dbp/GO-1/Au), and 10.157 mg L⁻¹ (Zn-H₄dbp/GO-5/Au) [98]. Although the bare Au electrode exhibited the lowest LOD (1.882 mg L⁻¹), the Zn-H₄dbp/Au electrode emerged as the optimal balance of sensitivity, selectivity, and cost-effectiveness, underscoring its potential as an efficient Cr(VI) sensor.

While sensors such as activated glassy carbon electrodes (GCEs) achieve lower Cr(VI) detection limits (e.g., 0.0052 mg L⁻¹), their relatively narrow linear ranges (0.02–13.00 mg L⁻¹) hinder their application in environments requiring broader concentration monitoring (**Table S7**). In contrast, although the Zn-H₄dbp/Au sensor has a higher limit of detection, it offers a well-balanced performance by combining adequate sensitivity with an extended linear range [99]. This makes it particularly effective for Cr(VI) detection in industrial and environmental settings with high contamination levels. With further optimization of materials and interfaces, this platform has the potential to meet or exceed regulatory standards, establishing it as a robust, scalable solution for next-generation Cr(VI) sensing technologies.

The insulating nature of GO disrupts electron transfer pathways, blocks active sites, and competes with Cr(VI) for adsorption sites, thereby impairing the electrochemical detection performance of Zn-H₄dbp/GO composites [100]. Although these composites benefit from complementary material properties for adsorption, the pristine Zn-H₄dbp/Au electrode maintains superior detection capability due to its unimpeded active site accessibility and optimized conductive network, which facilitate efficient charge transfer and enhanced sensitivity. To mitigate the insulating nature of GO in Zn-H₄dbp/GO composites, strategies such as incorporating conductive polymers (e.g., polyaniline or polypyrrole) can enhance conductivity while introducing additional redox-active sites [101]. Further improvements can be achieved by reducing GO to rGO (reduced graphene oxide) and optimizing its loading percentage, which enhances charge transfer efficiency and active site accessibility [102]. These modifications could significantly improve the electrochemical performance of the composite for Cr(VI) detection.

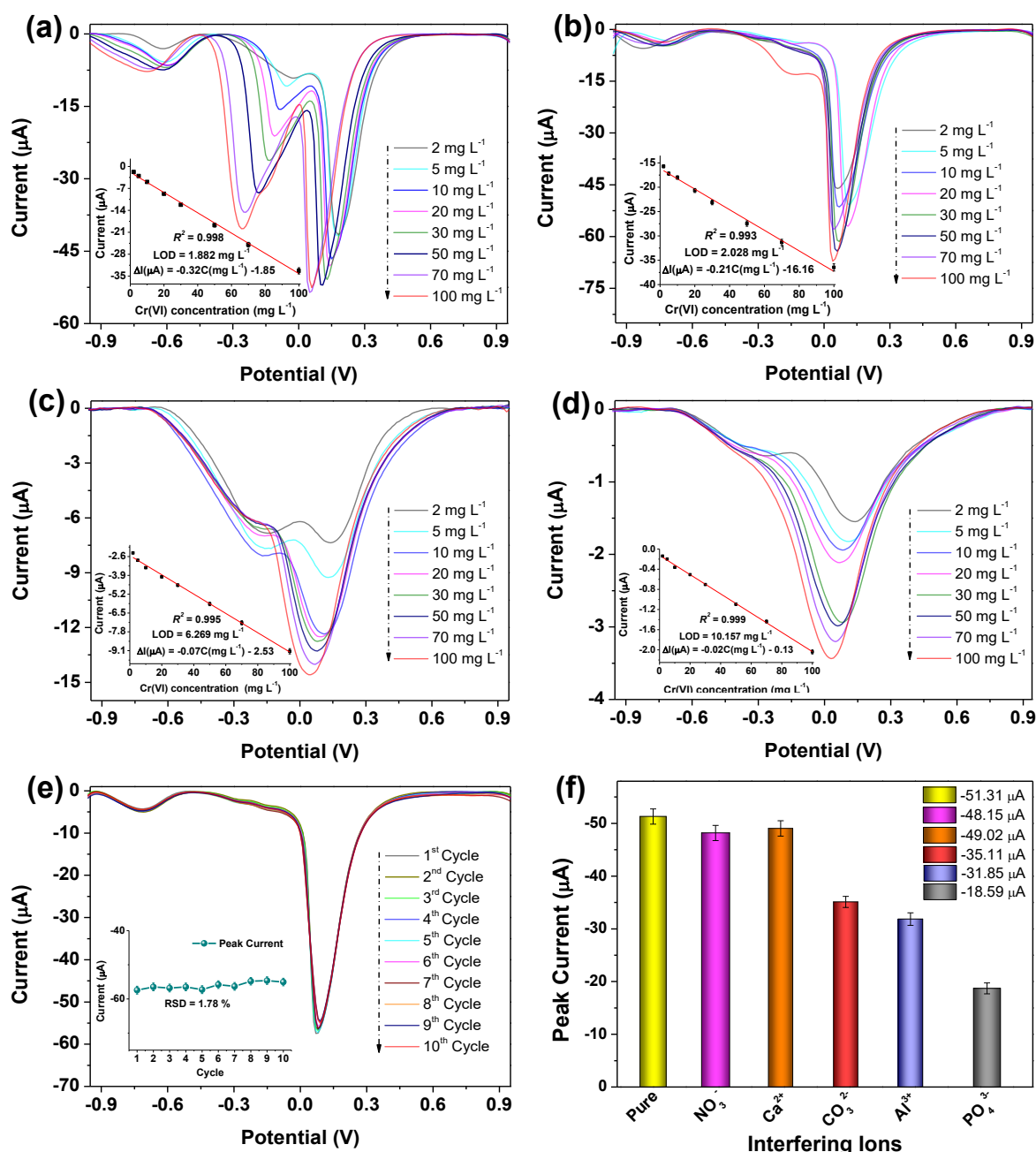


Fig. 6. SWV reduction of Cr(VI) analyte by: (a) Bare Au electrode, (b) Zn-H₄dbp/Au, (c) Zn-H₄dbp-GO-1/Au, and (d) Zn-H₄dbp-GO-5/Au; reproducibility measurements of Zn-H₄dbp/Au sensor (e) SWV spectrum for 10 cycles (inset: cycle versus current plot), (f) influence of coexisting ions on Cr(VI) SWV detection by Zn-H₄dbp/Au.

The Zn-H₄dbp/Au electrode exhibited excellent operational stability and reusability, as demonstrated by ten consecutive SWV measurements in a 10 mg L⁻¹ Cr(VI) solution under identical conditions (Fig. 6e). The peak current showed high consistency, with less than 2%

variation and a low relative standard deviation (RSD) of 1.78% (inset **Fig. 6e**), confirming reliable and repeatable performance for long-term monitoring [103].

To assess selectivity, the sensor was tested in the presence of 0.5 mol L⁻¹ common coexisting ions (NO₃⁻, Ca²⁺, CO₃²⁻, Al³⁺, and PO₄³⁻) (**Fig. 6f**) [32]. The baseline peak current for Cr(VI) alone was -51.31 μA. Minor signal reductions occurred with NO₃⁻ (-48.15 μA; 6.16% decrease) and Ca²⁺ (-49.02 μA; 4.46% decrease), suggesting negligible interference. In contrast, CO₃²⁻ (-35.11 μA; 31.57% decrease) and Al³⁺ (-31.85 μA; 37.93% decrease) caused moderate interference, likely due to competitive adsorption or electrostatic interactions. The most severe suppression occurred with PO₄³⁻ (-18.59 μA; 63.78% decrease), attributed to phosphate's strong binding affinity or surface fouling, which restricted Cr(VI) access to electroactive sites.

These results highlight the electrode's robust reproducibility and resistance to most interfering ions, though phosphate-rich environments require caution due to significant signal suppression.

4. Conclusion

In this study, a Zn-based MOF (Zn-H₄dbp) and its graphene oxide (GO) composite were developed for efficient Cr(VI) removal and detection in water. The Zn-H₄dbp/GO-5 composite (5 wt% GO) exhibited a remarkable Cr(VI) adsorption capacity of 311.8 mg g⁻¹, surpassing the performance of its individual components and many reported materials. Adsorption behavior followed the Freundlich isotherm and PSO kinetics, suggesting multilayer chemisorption. Ionic strength and coexisting ions influenced adsorption, with NaCl reducing electrostatic attraction and NO₃⁻ showing notable competition.

For detection, square wave voltammetry (SWV) revealed that Zn-H₄dbp/Au outperformed GO-containing electrodes, achieving higher sensitivity and current density due to superior electron transfer. The limit of detection (LOD) of 2.03 mg L⁻¹ further demonstrated the practicality of Zn-H₄dbp/Au. The electrode also demonstrated exceptional reusability (10 consecutive cycles, RSD = 1.78%) and selectivity, showing minimal interference from NO₃⁻

and Ca^{2+} but a significant signal suppression by PO_4^{3-} (63.78% reduction) due to competitive adsorption. In summary, Zn-H₄dbp/GO-5 is optimal for Cr(VI) adsorption, while Zn-H₄dbp/Au enables stable, sensitive detection, collectively offering a promising solution for industrial wastewater treatment.

CRedit authorship contribution statement.

A.K.; conceptualization, methodology, investigation, formal analysis, visualization, writing—original draft preparation, **T.-T. D. P.**, **A. M.**, **G. M.**; investigation, visualization, **S. C.**; resources, **J.P.**; conceptualization, supervision, funding acquisition, administration, writing — review & editing. All authors have read and agreed to the published version of the manuscript.

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