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Decoupling Steric-Dependent Adsorption Mechanisms in "Covalent-Ionic" Dual-Orthogonal Crosslinked GO/CS Hydrogels for Efficient Dye Sequestration

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Abstract:

Bulk hydrogel adsorbents show great promise in water remediation, yet overcoming the intrinsic contradiction between mechanical skeleton stability and high-density active sites remains a core challenge. Herein, a novel "covalent-ionic" dual-orthogonal crosslinking strategy based on sodium tripolyphosphate (TPP) and genipin was proposed to construct hierarchical mesoporous graphene oxide/chitosan (GO/CS) composite hydrogels. Compared to traditional highly toxic single-crosslinked systems, this strategy achieves robust spatial confinement of GO sheets while preserving abundant polar adsorption sites. By integrating comprehensive characterizations (SEM, BET, XRD, FT-IR, Raman, and XPS), the microscopic physicochemical synergistic adsorption mechanisms of the hydrogel toward planar methylene blue (MB) and bulky malachite green (MG) were

systematically elucidated. The results suggest a strong steric-dependent interfacial behavior: the capture of MB primarily relies on face-to-face π - π conjugated stacking with the GO basal plane and localized charge transfer, whereas the adsorption of sterically hindered MG is dominantly driven by Coulombic electrostatic attraction and hydrogen bonding provided by deprotonated carboxyl and polar nitrogen sites. Furthermore, the hydrogel maintained over 80% of its retention capacity after five consecutive adsorption-desorption cycles without macroscopic structural deterioration or GO leakage. This study offers an engineering solution to the solid-liquid separation difficulties of powdered adsorbents and establishes a theoretical paradigm for steric-dependent confined adsorption in complex polymer networks.

Keywords: Chitosan; Adsorption; Dual-orthogonal crosslinking

1. Introduction

The unregulated discharge of industrial wastewater introduces a massive amount of synthetic dyes into surface water ecosystems, evolving into a severe global environmental crisis [1, 2]. Among various organic pollutants, typical cationic dyes represented by methylene blue (MB, phenothiazine class) and malachite green (MG, triphenylmethane class) are extensively utilized in the fine chemical and textile industries [3]. The highly conjugated aromatic topological structures and dense delocalized electron clouds within these dye molecules endow them with strong intrinsic resistance to natural photolysis and enzymatic degradation [4]. Experimental and ecological monitoring confirm that high concentrations of dye wastewater not only significantly reduce the light transmittance of water bodies and inhibit aquatic photosynthesis, but their highly persistent retention in the aqueous phase also facilitates bioaccumulation through the food chain. These macromolecules and their aromatic amine degradation intermediates exhibit strong mutagenicity and targeted hepatorenal toxicity to aquatic organisms and humans [5, 6].

To mitigate the aforementioned ecotoxicological risks, although conventional purification strategies such as membrane separation, advanced oxidation, and ion exchange have been developed, interfacial adsorption has been widely established as the core technology for dye sequestration owing to its outstanding cost-effectiveness, extremely low energy requirements, and the physicochemical advantage of generating no toxic halogenated byproducts [7, 8]. However, commercial powdered adsorbents, represented by activated carbon and inorganic zeolites, are facing severe performance bottlenecks in practical engineering. On the one hand, the pore structures of these materials are predominantly microporous (< 2 nm), which induces severe mass transfer steric hindrance when encountering bulky organic dye macromolecules, leading to an extremely low saturated adsorption capacity for target pollutants [9, 10]. On the other hand, micron-sized powder particles are notoriously difficult to macroscopically separate from the solid-liquid phase during high-throughput industrial wastewater treatment, easily triggering irrecoverable secondary sludge pollution and nanotoxicity [11, 12]. Therefore, constructing a bulk polymeric adsorption matrix that simultaneously integrates 3D interconnected mesoscopic channels, a high density of active binding sites, and excellent macroscopic shear resistance constitutes a critical technical barrier that urgently needs to be overcome in current environmental remediation materials science [13].

In this context, natural polysaccharide hydrogels provide an ideal topological channel for the ultrafast cross-interface mass transfer of macromolecular solutes, owing to their 3D spatially crosslinked networks and intrinsic superhydrophilic properties [14]. As a typical representative of such matrices, the highly dense distribution of free primary amines ($-NH_2$) and hydroxyls ($-OH$) on the polymeric backbone of chitosan (CS) provides abundant hydrogen bonding and electrostatic anchoring sites for the targeted capture of cationic dyes [15]. However, single-component CS hydrogels suffer from low cohesive energy density and are highly susceptible to protonation-induced swelling and structural collapse in acidic wastewater. Moreover, their monotonic active site configuration struggles to achieve efficient sequestration in

complex industrial effluents [16, 17]. To deeply decouple this limitation, introducing 2D graphene oxide (GO) for polymeric network reconstruction has been proven to be a highly promising nano-modification strategy [18, 19]. GO not only endows the composite system with an ultrahigh theoretical surface area ($\sim 2630 \text{ m}^2/\text{g}$), but its basal planes and edges enriched with highly electronegative functional groups (e.g., carboxyl and epoxy groups) profoundly broaden the chemical boundaries of electrostatic neutralization and dipole-dipole interactions [20]. The synergistic effect between the two at the microscopic scale is particularly remarkable: the long polymeric chains of CS provide strong steric hindrance through physical intercalation, effectively preventing the irreversible restacking of GO sheets in the aqueous phase triggered by π - π stacking and van der Waals forces; conversely, the rigid 2D carbon skeleton of GO acts as a nano-reinforcing phase, substantially enhancing the rheological modulus and physical rigidity of the polysaccharide network [21, 22]. This multidimensional coupling based on scale and chemical state lays a solid material foundation for constructing ultrahigh-capacity adsorption platforms [23].

Although the design of porous matrices tends to be theoretically perfect, the excessive pursuit of extreme porosity inevitably compromises the structural stability of composite hydrogels. Existing conventional physically crosslinked GO/CS hydrogels are prone to excessive swelling when subjected to high-frequency desorption-elution cycles, triggering the collapse of internal mesoporous channels and even leading to the exfoliation and leakage of 2D GO sheets [24]. To remedy these mechanical defects, traditional processes frequently introduce chemical crosslinkers such as glutaraldehyde (GA). However, while leaving severe biological toxicity, this strategy induces a fatal intrinsic structural paradox: GA excessively consumes the primary amines on the CS chains via a non-selective Schiff base reaction [25, 26]. This excessive occupation of the dominant dye adsorption sites directly results in a precipitous decline in the macroscopic adsorption capacity of the modified materials [27]. Thus, how to precisely decouple the structural contradiction between a "dense anti-fatigue skeleton" and a "high density of free active adsorption sites" has emerged

as a core scientific challenge restricting the long-term engineering application of bulk hydrogels [28].

To fundamentally break through the aforementioned intrinsic contradictions, this study abandons the highly toxic and non-selective single covalent crosslinking mechanism, proposing and constructing for the first time a "covalent-ionic" dual-orthogonal crosslinked network strategy based on genipin (a natural, low-toxicity biogenic crosslinker) and sodium tripolyphosphate (TPP, a polyanionic crosslinker). The dynamic topological evolution logic of this strategy is as follows: in the initial stage of gelation, the multivalent anions ($\text{P}_3\text{O}_{10}^{5-}$) released by TPP preferentially trigger an ultrafast dynamic electrostatic assembly (ionotropic gelation) with the protonated amines ($-\text{NH}^{3+}$) on the CS skeleton, instantaneously locking the primary mesoporous support backbone [29]; subsequently, under mild boundary conditions, genipin *in situ* sutures a covalent heterocyclic network with high hydraulic shear resistance through specific nucleophilic attack and Michael addition reactions [30]. This dual-orthogonal network not only achieves permanent spatial confinement of the GO sheets in physical space but also precisely circumvents the excessive consumption of oxygen-containing polar functional groups at the chemical level. Based on this model, highly stable GO/CS dual-crosslinked composite hydrogels were systematically synthesized. On the basis of establishing thermodynamic boundaries, the hydrodynamic mass transfer resistance was strictly decoupled via the Bangham model and intra-particle diffusion equations. By deeply integrating X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, the multiple synergistic mechanisms of Coulombic electrostatic attraction, hydrogen bond evolution, and π - π conjugation were semi-quantitatively elucidated at the atomic orbital scale. Through high-intensity cyclic regeneration verification, this study aims to provide concrete physicochemical evidence for elucidating the hierarchical confined adsorption mechanisms within complex polymeric porous networks and to establish a theoretical paradigm for the topological design of next-generation durable water remediation materials.

2. Materials and Methods

2.1 Materials and reagents

High-purity graphite powder (99% purity) and chitosan (CS, degree of deacetylation $\geq 85\%$) were purchased from Shanghai Macklin Biochemical Co., Ltd., China. Genipin and sodium tripolyphosphate (TPP) were supplied by Anhui Zesheng Technology Co., Ltd., China. Methylene blue (MB), malachite green (MG), and other analytical-grade reagents were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Graphene oxide (GO) was synthesized via a modified Hummers method [31]. All aqueous solutions were prepared using ultrapure water.

2.2 Preparation of the dual-crosslinked GO/CS hydrogel

A sequential gelation strategy was employed to fabricate the GO/CS composite hydrogel. Initially, 3.0 g of CS was dissolved in 100 mL of an aqueous acetic acid solution (2.5% v/v) and stirred for 15 h to ensure complete protonation of the amino groups. Subsequently, 0.7 g of GO was ultrasonically dispersed into the CS solution. During the primary ionic crosslinking stage, a TPP solution (1.0% w/v) was added dropwise under vigorous stirring for 30 min to drive the ionotropic gelation. After washing, the precursor was immersed in a 0.1 wt% genipin solution for 4 h to trigger the secondary covalent crosslinking [32]. The resulting hydrogel was washed to a neutral pH and lyophilized at $-50\text{ }^{\circ}\text{C}$ for 48 h. The synthetic mechanism is illustrated in Scheme 1.

2.3 Characterizations

To investigate the multiscale morphological and physicochemical evolution of GO, pristine CS, and the GO/CS composite hydrogels (before and after dye adsorption), comprehensive characterizations were conducted. The 3D porous morphology was observed using a field-emission scanning electron microscope (FE-SEM, Zeiss Gemini Sigma 300 VP) at an accelerating voltage of 5.0 kV. The specific surface area

and pore size distribution were quantitatively determined from N₂ adsorption-desorption isotherms at 77 K (Micro 3Flex) using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Surface chemical configurations were identified via Fourier transform infrared spectroscopy (FT-IR, Nicolet iS5, KBr pellet method, scanning range of 400–4000 cm⁻¹) and Raman spectroscopy (LabRAM HR Evolution, 633 nm laser excitation). Crystallographic properties were acquired using an X-ray diffractometer (XRD, Rigaku, Cu-K_α radiation, $\lambda = 0.154$ nm) scanning from 10° to 60° at a rate of 10°/min. Furthermore, X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi⁺) was utilized to profoundly probe the surface elemental compositions and high-resolution chemical states, with all binding energies calibrated to the adventitious C 1s peak at 284.8 eV .

2.4 Batch adsorption and desorption experiments

All batch adsorption experiments were performed in a temperature-controlled water bath shaker (SHA-CA) at a constant speed of 150 rpm to systematically evaluate the boundaries of critical operational parameters on the equilibrium adsorption capacity (q_e , mg/g) and removal efficiency. Specifically, various dosages of the GO/CS hydrogel (0.1–2.0 g/L for MB; 1.6–3.6 g/L for MG) were introduced into 50 mL of target dye solutions. The initial pH of the working solutions (2.0–10.0) was precisely adjusted using 0.1 M HCl and NaOH.

For kinetic evaluations, 0.1 g of the adsorbent was dispersed in 50 mL of dye solutions (50 mg/L for MB; 100 mg/L for MG) at a constant temperature of 20 °C, and the residual concentrations were quantified at predetermined time intervals (0.5–180 min). Isotherm and thermodynamic studies were conducted across a temperature gradient from 293 K to 333 K by varying the initial dye concentrations (20–100 mg/L for MB; 100–200 mg/L for MG). Upon completion, the residual dye concentrations were determined by measuring the absorbance at their maximum absorption wavelengths (664 nm for MB and 618 nm for MG) using a UV-Vis

spectrophotometer.

To assess the long-term engineering regeneration feasibility, cyclic adsorption-desorption tests were executed. The dye-loaded GO/CS hydrogels were eluted in 50 mL of absolute ethanol (the optimal eluent validated in preliminary experiments) for 60 min, repeatedly washed with ultrapure water, and subjected to five consecutive adsorption-desorption cycles.

2.5 Data processing and classic adsorption model evaluation

The equilibrium adsorption data were fitted using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) models [33, 34]. Mass transfer behaviors were analyzed via the pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Bangham kinetic equations to evaluate the mass transfer resistance [35]. The goodness-of-fit was determined by the coefficient of determination (R^2). The relevant linearized mathematical expressions and calculation formulas for thermodynamic parameters such as Gibbs free energy (ΔG) are detailed in the Supplementary Information.

3. Results and Discussion

3.1 Microscopic morphology and pore evolution of the dual-crosslinked network

Compared to the typical 2D disordered wrinkled stacking morphology of pristine GO (Fig. 1A), the GO/CS composite *in situ* assembled into a highly interconnected 3D porous network architecture under the dual crosslinking of TPP and genipin (Fig. 1B). SEM images reveal that its macroscopic pore sizes are uniformly distributed within the 50–200 μm range. The formation of this macroscopic skeleton not only endows the material with excellent hydrodynamic support but also provides broad fluid channels for the preliminary permeation of dye molecules in the aqueous phase [36].

X-ray diffraction (XRD) patterns (Fig. 1C) corroborated the microscopic assembly mechanism of this topological network from a crystallographic perspective. As

depicted in Fig. 2C, the sharp characteristic diffraction peak of pristine GO at $2\theta = 10.1^\circ$ almost completely vanished in the composite hydrogel [37]. This crystallographic phenomenon provides direct physical evidence that during the gelation process, the robust intercalation of long CS polymer chains and the anchoring effect of the dual network achieved the complete exfoliation of GO sheets, fundamentally suppressing the interlayer restacking tendency of the 2D nanomaterials driven by van der Waals forces. Concurrently, the semi-crystalline characteristic peak of pure CS at approximately $2\theta = 20.0^\circ$ also underwent significant broadening and intensity attenuation after compounding, confirming that the strong interfacial non-covalent interactions and covalent crosslinking reactions disrupted the orderly arrangement of the polymer segments.

To further quantify the hierarchical pore evolution of this exfoliated topological network, precise characterizations were performed via N_2 adsorption-desorption isotherms (Fig. 1D and 1E). The isotherm of the GO/CS composite exhibited a prominent Type IV characteristic with an H3 hysteresis loop, confirming the presence of an abundant mesoporous structure. The test results indicated that compared to the highly restacked pristine GO (with a specific surface area of merely $32.19 \text{ m}^2/\text{g}$), the specific surface area of the dual-crosslinked GO/CS hydrogel substantially leaped to $58.74 \text{ m}^2/\text{g}$, with a total pore volume reaching $0.342 \text{ cm}^3/\text{g}$ and pore sizes densely concentrated in the typical mesoporous range of 23.3 nm . This hierarchical porous network architecture, progressively transitioning from macroscopic macropores ($50\text{--}200 \text{ }\mu\text{m}$) to mesoscopic nanopores (23.3 nm), not only effectively exposed the physically confined oxygen- and nitrogen-containing active sites but also thermodynamically mitigated the steric hindrance for the intra-particle diffusion of bulky MB and MG molecules, thereby providing the structural prerequisites for subsequent high-capacity interfacial capture .

3.2 Reconstruction of surface chemical configurations and localized electronic states

Fourier transform infrared (FT-IR) and Raman spectroscopy provided complementary vibrational spectroscopic evidence for the formation of the dual-network skeleton. The FT-IR spectra (Fig. 2A) illustrate that upon the formation of the GO/CS composite hydrogel, the intensity of the carboxyl C=O peak originally located at $\sim 1730\text{ cm}^{-1}$ on GO significantly attenuated. Concurrently, new robust absorption bands emerged at $\sim 1640\text{ cm}^{-1}$ and $\sim 1550\text{ cm}^{-1}$, which are assigned to the Amide I band and the electrostatic attraction between carboxylate anions ($-\text{COO}^-$) and protonated amines ($-\text{NH}_3^+$), respectively [38,]. Furthermore, the broad absorption band at $\sim 3420\text{ cm}^{-1}$, corresponding to the overlapping stretching vibrations of $-\text{OH}$ and $-\text{NH}_2$, shifted to lower wavenumbers ($\sim 3400\text{ cm}^{-1}$) and notably broadened [39]. These synergistic spectral variations confirm the successful construction of a robust electrostatic attraction and intermolecular hydrogen bonding network between the oxygen-rich domains of GO and the polycationic CS chains.

Meanwhile, Raman spectra (Fig. 2B) corroborated this intense chemical crosslinking from the dimension of the underlying carbon skeleton. In the spectrum of pristine GO, the intensity ratio (I_D/I_G) between the D band ($\sim 1350\text{ cm}^{-1}$), which corresponds to structural disorder and defects, and the G band ($\sim 1590\text{ cm}^{-1}$)[24], representing the in-plane sp^2 carbon hybridization, was 0.82. Following the composite formation of the GO/CS hydrogel, this ratio significantly increased to 1.05. This substantial elevation in defect density does not imply material degradation; rather, it indicates that the CS chains (especially the highly reactive free amines and hydroxyls) underwent profound spatial intercalation and chemical bonding with the basal planes and edge regions of GO, driving the conversion of a fraction of planar sp^2 conjugated carbons into sp^3 topological defects [40]. This functionalization-induced defect-rich carbon skeleton not only introduces a higher density of 3D binding sites into the hydrogel but also provides a crucial structural foundation for the subsequent π - π optical shielding effect triggered during dye adsorption.

To further unravel the atomic-level orbital reconstruction underpinning the aforementioned chemical bond reorganization, X-ray photoelectron spectroscopy (XPS) was employed. In the core-level C1s spectrum (Fig. 3), the integral area of oxygenated carbon species decreased significantly after gelation, indicating that the intercalation of CS remarkably modified the localized electronic states on the surface of the GO sheets [41]. Simultaneously, in the high-resolution N 1s spectrum, the multistate superposition of energy levels robustly supported the non-covalent/covalent orthogonal construction of the crosslinked network. Apart from the free amines of the chitosan backbone (~ 399.0 eV, $-\text{NH}_2$), the spectrum clearly differentiated two high-binding-energy peaks located at ~ 399.9 eV and 401.75 eV. The former is assigned to the amide groups ($-\text{NH}-\text{C}=\text{O}$) formed via carboxyl condensation, providing direct evidence of covalent crosslinking at the atomic orbital scale; the latter is unambiguously attributed to the protonated amine state ($-\text{NH}_3^+$) generated by electrostatic neutralization, confirming the establishment of strong Coulombic electrostatic neutralization axes between the oxygen-containing functional groups on the GO basal planes and the CS chains [42]. The evolution of these multistate superimposed electronic states constitutes a compelling characterization of the synergistic occurrence of chemical bonding and physical confinement within the system.

3.3 Evaluation of macroscopic adsorption performance and exploration of boundary conditions

To verify the synergistic enhancement of the dual-crosslinked matrix at the macroscopic mass transfer level, this study first horizontally compared the macroscopic dye sequestration performance of pristine GO, the single CS skeleton, and the GO/CS composite hydrogel (detailed comparative data are provided in the Supplementary Information, Fig. S1). Experimental results confirmed that although pristine GO sheets possess an ultrahigh theoretical specific surface area, their irreversible interlayer restacking in the aqueous environment led to severe masking of

active sites. Meanwhile, the single CS hydrogel was constrained by its extremely low cohesive energy density and limited mass transfer specific surface area, resulting in an inferior adsorption capacity. In stark contrast, relying on the robust physical confinement of the 3D mesoporous channels and the highly efficient exposure of polar active sites, the GO/CS dual-crosslinked composite system exhibited a remarkable performance leap in adsorption capacity.

Based on this optimal material matrix, to establish the optimal operational boundaries for the mass transfer system, the macroscopic effects of single variables—including adsorbent dosage, pH, temperature, contact time, and initial concentration—on the adsorption performance were systematically investigated (detailed data and analyses are presented in Fig. S2–S6). Among the core environmental disturbance variables, the pH sensitivity tests revealed that the sequestration capacities for both MB and MG reached their maxima in the weakly acidic to near-neutral range (pH = 6). This is primarily attributed to the deprotonation-induced reconfiguration of the carboxyl groups on the GO/CS skeleton (forming -COO^-) as the pH increased, which effectively mitigated the electrostatic repulsion under strongly acidic conditions and thereby amplified the Coulombic attraction of the porous matrix toward the cationic dyes [43]. Furthermore, thermodynamic calculations (Table 1 and Fig. S7–S8) corroborated that the adsorption enthalpy changes (ΔH) for MB and MG were +21.84 kJ/mol and +40.46 kJ/mol, respectively, confirming the endothermic nature of the processes. The Gibbs free energy data ($\Delta G < 0$) indicated that elevated temperatures facilitate overcoming the solvation dehydration barrier at the multiphase interface, thereby driving the spontaneous progression of the physicochemical adsorption [44].

The fitting of the isotherm models (Table 2 and Fig. S9–S10) further elucidated the energy distribution characteristics at the solid-liquid interface. The adsorption trajectory of MG converged highly with the Freundlich model ($R^2 = 0.9911$), indicating that the dual-crosslinked network endowed the surface binding energy with heterogeneity, leaning toward multilayer composite adsorption; the theoretical

maximum monolayer adsorption capacity derived from the Langmuir model reached 114.94 mg/g. Conversely, the isotherm of MB exhibited excellent fits with both the Temkin and Dubinin-Radushkevich (D-R) models ($R^2=0.9739$ and 0.9735 , respectively). Notably, the mean free energy of adsorption (E) calculated from the D-R model was 8.96 kJ/mol. Crucially, as this value exceeds the classic 8.0 kJ/mol threshold, it thermodynamically validates that the targeted capture of MB is not merely governed by weak non-localized van der Waals forces. Instead, it is dominantly driven by chemical adsorption processes—such as robust electrostatic interactions and ion exchange—which synergistically couple with the physical confinement of the mesoscopic pores [45].

The analysis of kinetic resistance (Table 3 and Fig. S11–S12) precisely decoupled the confined mass transfer mechanisms within the channels. The intra-particle diffusion model exhibited a high goodness-of-fit for MB with a non-zero intercept, delineating a stage-wise transition from rapid mass transfer across the external liquid film to restricted diffusion within the micro/mesopores. Notably, the dynamic diffusion trajectory of MG aligned highly with the Bangham pore kinetic model, providing compelling evidence that the penetration rate of the sterically hindered dye into the deep layers of the material is not solely controlled by physicochemical bonding; rather, it is deeply restricted by the diffusion resistance of the hierarchical interconnected channels (~ 23.3 nm) within the composite matrix.

3.4 Full-scale decoupling of the microscopic synergistic adsorption mechanisms

The discrepancy in macroscopic adsorption performance intrinsically originates from the interfacial reconstruction of microstructures and electronic states between the dye molecules and the material. Combining the aforementioned thermodynamic and kinetic boundary evaluations, this study integrates multi-scale characterization techniques to systematically propose a steric-dependent physicochemical synergistic adsorption model (the comprehensive mechanistic panoramic view is illustrated in Scheme 2). This schematic diagram intuitively unveils that the capture of cationic

dyes by the GO/CS dual-crosslinked hydrogel has completely transcended the scope of singular physical pore interception. Instead, it manifests as a macroscopic-to-microscopic cascading response process: namely, mesoporous confinement, electrostatic/hydrogen-bond anchoring driven by the oxygen-/nitrogen-containing polar groups at the phase interface, and steric-dependent π - π delocalization which is profoundly governed by the spatial topological configurations of the dyes. The in-depth spectroscopic decoupling of this synergistic mechanism across these three scales is elucidated as follows.

At the level of physical confinement and topological structure, the evolution of mesoporous channels provides direct evidence for interfacial mass transfer and physical interception. Morphological analyses (Fig. 4A and 4B) reveal that upon the adsorption of MB and MG, the original highly ordered porous network of the composite hydrogel underwent localized shrinkage, with some mesoporous channels experiencing restricted blockage. These morphological features align with the BET results (Fig. 4C and 4D): after reaching adsorption saturation, the specific surface area of the material sharply declined from 58.74 m²/g to 32.58 m²/g, and the average pore size shrank from 23.3 nm to approximately 13 nm. This significant reduction in pore parameters offers static physical evidence for the previously discussed intra-particle restricted diffusion mechanism, indicating that the bulky dye macromolecules were effectively anchored within the network via physical confinement effects. Simultaneously, the XRD patterns (Fig. 4F) corroborate this microscopic filling process from a crystallographic perspective. Post-adsorption, the characteristic diffraction peaks of the original GO/CS skeleton at $2\theta = 10.1^\circ$ and 20.0° significantly attenuated, accompanied by an elevation in amorphous scattering features across the baseline. This suggests that as the bulky dye molecules intercalated into the porous fluidic channels, they underwent multi-site binding with the skeletal functional groups, spatially perturbing the orderly stacking of the pristine graphene oxide sheets and thereby locally reducing the crystalline ordering of the material [46].

At the level of chemical bonding and non-covalent interactions, the shifting of

phase-interfacial polar chemical bonds and the delocalized reconstruction of the carbon substrate played a dominant role. As shown in the FT-IR spectra (Fig. 5A), after dye adsorption, the broad absorption bands around $\sim 3400\text{ cm}^{-1}$ corresponding to the stretching vibrations of -OH and -NH₂ exhibited a pronounced redshift and broadening [47]. This robustly confirms that the highly active oxygen/nitrogen sites on the skeleton and the cationic dyes successfully constructed a dense intermolecular hydrogen-bonding network and Coulombic electrostatic neutralization axes. More critically, the Raman spectra (Fig. 5B) provide definitive optical criteria for the steric-regulated non-covalent mechanism. The defect density ratio (I_D/I_G) of the pristine GO/CS hydrogel was approximately 1.05. Strikingly, following the adsorption of planar MB, this ratio experienced a precipitous cliff-like drop (plummeting to ~ 0.27). This characteristic "extreme attenuation of defect rate" hints at an exceptionally strong π - π stacking effect: the highly coplanar phenothiazine conjugated structure of MB can form an ultimate face-to-face stacking with the 2D GO basal planes. This intimate electron delocalization extensively "masks" the sp^3 topological defect sites of the carbon skeleton at the optical detection level [48]. In sharp contrast, MG possesses a massive triphenylmethane non-planar steric configuration; its enormous steric hindrance forcibly widens the physical distance between its aromatic rings and the GO substrate, restricting the π - π electron conjugation. Consequently, the reduction in I_D/I_G after MG adsorption was extremely limited (only slightly decreasing to ~ 0.9), fundamentally failing to achieve massive optical shielding of the defect sites.

At the atomic orbital scale, the XPS spectra (Fig. 6) profoundly unravel the charge transfer and electronic state reconstruction during the phase-interfacial interaction. Following the adsorption of planar MB, the primary binding energy peaks of N 1s (located at approximately 398.8 eV, 399.6 eV, and 401.2 eV) all shifted negatively toward lower energy fields, indicating a charge transfer from the electron-rich conjugated system of MB to the matrix [49]. Conversely, upon the adsorption of sterically hindered MG, all chemical state binding energies of N 1s (located at

approximately 399.2 eV, 400.0 eV, and 401.95 eV) shifted positively toward higher energy fields. This constitutes the signature of typical Coulombic electrostatic attraction: the lone-pair electrons of the polar nitrogen atoms on the skeleton are strongly attracted toward the electropositive center of the MG molecule. Furthermore, as depicted in the lower right of Fig. 8, the multi-component deconvolution of the O 1s spectrum after MG adsorption (emerging complex sub-peaks at ~531.0 eV, 532.0 eV, and 532.7 eV), coupled with the precipitous drop in the proportion of HO-C=O in the C 1s spectrum (~288.5–288.6 eV), further corroborates that the oxygen-containing groups deeply participated in the electrostatic neutralization and the reconstruction of the robust hydrogen-bonding network [50].

3.5 Long-term cyclic regeneration performance and engineering feasibility verification

The industrial application potential of bulk adsorbents highly depends on their structural stability and long-term desorption efficiency. Prior to executing continuous cyclic tests, this study first systematically evaluated the desorption efficiencies of dye-loaded hydrogels using various eluents (ethanol, HCl, water, and NaOH) (detailed data are provided in the Supplementary Information, Fig. S13). The results demonstrate that absolute ethanol exhibited superior elution performance for both MB and MG. This is primarily attributed to the intrinsic amphiphilic nature of ethanol: its polar hydroxyl group can form competitive hydrogen bonds with dye molecules, while its non-polar alkyl chain effectively weakens the hydrophobic associations between the dyes and the carbon skeleton, thereby driving dye desorption through a profound solvation effect [51].

Based on this optimal boundary condition, the GO/CS dual-crosslinked hydrogel was subjected to five consecutive batch adsorption-desorption cycles using absolute ethanol. As illustrated in Fig. 7, the removal efficiencies for both MB and MG remained above 80% after five cycles. Macroscopically, the hydrogel exhibited no volumetric shrinkage or fragmentation post-cycling; microscopically, no leakage of

2D GO sheets was detected in the eluent. This exceptional shear resistance and elution resilience benefit from the structural advantages of the "covalent-ionic" dual-crosslinked network. During the desorption process, the high polarity of absolute ethanol effectively disrupted the non-covalent π - π stacking network between the dyes and GO [52]. Concurrently, the rigid crosslinked backbone constructed by TPP and genipin not only locked the internal hierarchical channels but also effectively averted pore collapse, ensuring the re-exposure of active binding sites after desorption. The marginal decline in adsorption efficiency observed in the later stages of cycling is generally ascribed to the irreversible physical occupation of a minute fraction of high-energy sites within the deep micropores by dye molecules [53].

In summary, the GO/CS dual-crosslinked hydrogel demonstrated a capacity retention rate of over 80% during continuous operation. It should be noted that although this study primarily validated its reversible regenerability under batch operational boundaries, the outstanding macroscopic anti-fatigue stability of this dual-crosslinked bulk skeleton lays a solid material foundation for its future large-scale engineering applications in dynamic continuous-flow treatment systems.

4. Conclusions

In summary, a covalent–ionic dual-orthogonal crosslinked graphene oxide/chitosan bulk hydrogel, fabricated via tripolyphosphate and genipin, has been successfully established, which effectively circumvents the intractable solid–liquid separation bottleneck of conventional powdered adsorbents and the structural fragility of singly crosslinked networks. This orthogonal crosslinking architecture not only spatially confines two-dimensional GO sheets and prevents their aqueous restacking, but also constructs highly interconnected hierarchical mesoporous channels, thereby achieving an exceptional compromise between macroscopic shear resistance and a high density of accessible active sites. Comprehensive spectroscopic investigations further decouple the steric-dependent microscopic sequestration pathways, revealing a physico-chemical synergistic process dominated by chemisorption: planar methylene

blue primarily relies on physical pore confinement and intimate face-to-face π - π conjugated stacking, whereas the bulky, non-planar malachite green, hindered by steric constraints, shifts its binding toward strong Coulombic electrostatic attraction and hydrogen-bond anchoring driven by polar functional groups on the scaffold. Under absolute ethanol elution, the composite hydrogel retains over 80% of its adsorption capacity after five consecutive regeneration cycles. Although the current study focuses on batch-mode mechanistic validation, the remarkable cyclic resilience of this dual-crosslinked matrix provides a robust material foundation for its scalable implementation in dynamic continuous-flow wastewater treatment systems.

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Declaration of Competing Interest

The authors declare that there are no financial or personal conflicts of interest related to the research presented in this paper.

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Table 1. Thermodynamic parameters for the adsorption of MB and MG onto the GO/CS double-crosslinked hydrogel.

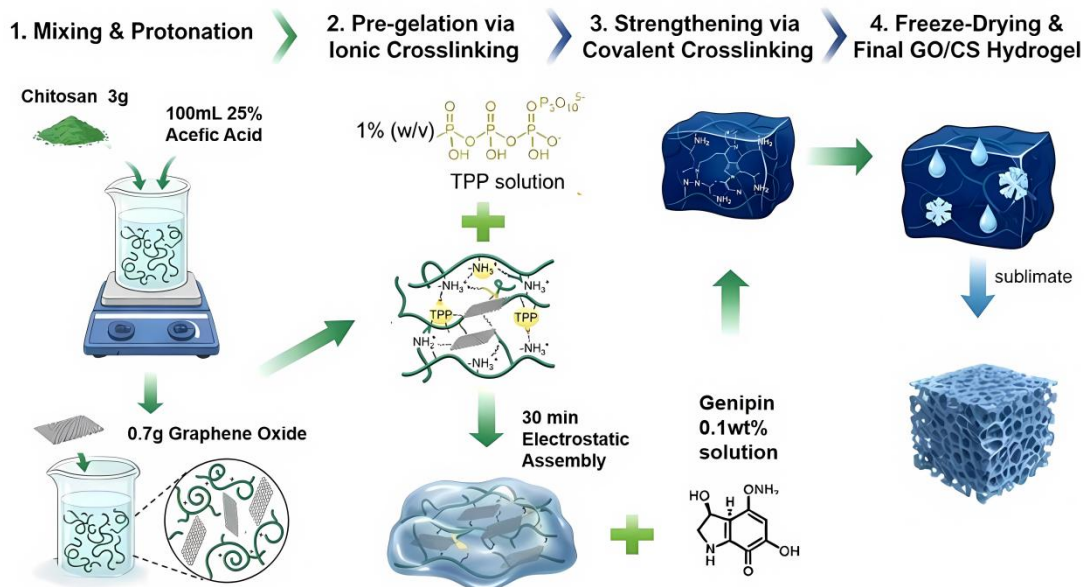
Dyes	T (K)	K_c	ΔG^0 (kJ/mol)	ΔS^0 (J/mol/K)	ΔH^0 (kJ/mol)	Equation	R^2
MB	293	1.53	-1034.54	88.79	21.844	$y = -2627.4x + 10.68$	0.8374
	303	2.11	-1878.64				
	313	2.56	-2449.32				
	323	2.51	-2476.35				
	333	2.65	-2698.78				
MG	293	3.86	-3289.60	169.34	40.46	$y = -4866.8x + 20.368$	0.9891
	303	4.21	-3624.76				
	313	4.76	-4061.86				
	323	5.37	-4517.87				
	333	5.77	-4855.59				

Table 2. Isotherm model fitting parameters depicting the surface binding energy distribution for MB and MG.

Isotherm models	Parameters	MB	MG
Langmuir	Equation	$y = 0.2287x - 0.0015$	$y = 0.0124x + 0.0087$
	q_{max} (mg/g)	43.7	114.94
	K_l (L/mg)	0.10	0.70
	R^2	0.887	0.9591
Freundlich	Equation	$y = 0.8012x + 1.8198$	$y = 0.4172x + 3.8759$
	K_F (mg/g · (1/mg) ^{1/n})	6.17	48.23
	n	1.25	2.40
	R^2	0.8832	0.9911
Temkin	Equation	$y = 18.772x - 4.5871$	$y = 29.334x + 45.697$
	K_T (L/mol)	0.78	4.75
	B_1	18.772	29.33
	R^2	0.9739	0.9747
Dubinin-Radushkevich	Equation	$y = -6E-09x - 4.908$	$y = -1E-09x - 7.4034$
	Q_m (mol/g)	1.09E-03	5.93E-04
	K_D (mol ² /kg ²)	6.22E-09	1.01E-09
	R^2	0.9735	0.882
	E (kJ/mol)	8.96	22.26

Table 3. Kinetic model fitting parameters revealing the interfacial mass transfer mechanisms of MB and MG.

Kinetic models	Parameters	MB	MG
Pseudo-first-order	Equation	$y = -0.2739x + 1.4939$	$y = -0.5662x + 0.5893$
	K_l (min^{-1})	0.63	1.30
	q_e (mg/g)	23.72	49.91
	R^2	0.9134	0.9512
	Equation	$y = 0.7155x - 1.7467$	$y = 0.3356x - 0.8302$
Pseudo-second-order	K_2 ($\text{g/ (mg} \cdot \text{min))}$	-0.001018	-0.0004836
	H ($\text{g/ (mg} \cdot \text{min))}$	0.000334	0.702
	R^2	0.9114	0.9052
	Equation	$y = 0.1982x + 21.248$	$y = 0.0518x + 49.39$
Intraparticle diffusion	K_{id} ($\text{mg/ (g} \cdot \text{min}^{-0.5})$)	0.1982	0.0518
	C (mg/g)	21.248	49.39
	R^2	0.9727	0.7584
	Equation	$y = 0.0687x - 0.0861$	$y = 0.0736x + 0.2729$
Bangham	α	0.0687	0.0736
	K_0 (mL/ (g/L))	0.9465	2.1614
	R^2	0.9107	0.979



Scheme 1. Schematic illustration of the fabrication strategy and double-crosslinking mechanism of the GO/CS hydrogel.

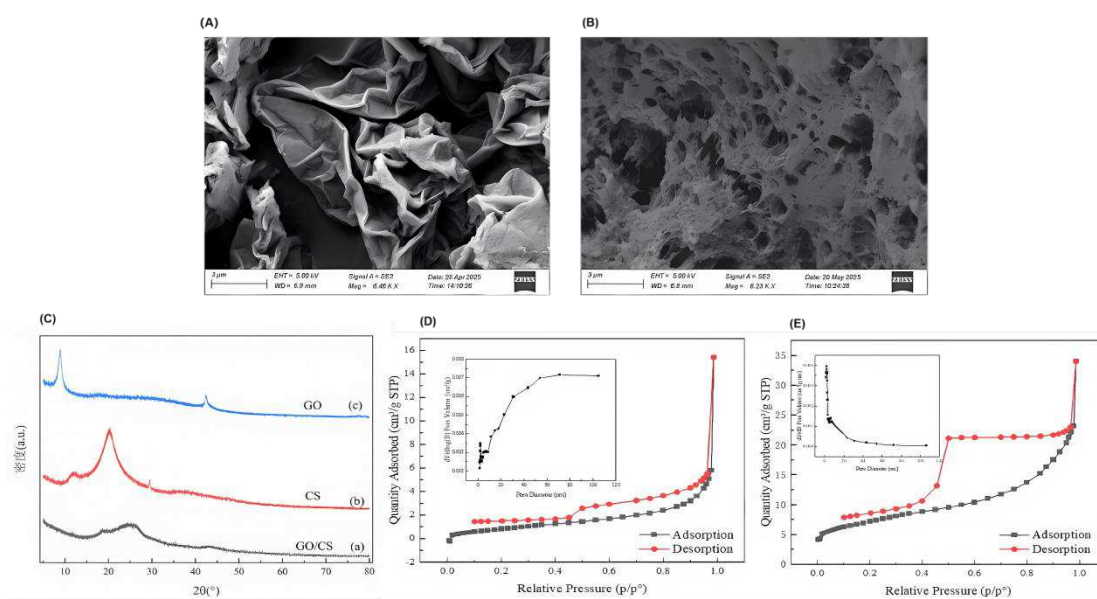


Fig. 1. Morphological and topological evolution of the GO/CS double-crosslinked skeleton. SEM images of (A) 2D GO nanosheets and (B) 3D GO/CS hydrogel; (C) XRD patterns of GO, pure CS, and GO/CS composites, indicating crystallographic reconstruction after compositing; Nitrogen adsorption-desorption isotherms of (D) pristine GO and (E) GO/CS hydrogel.

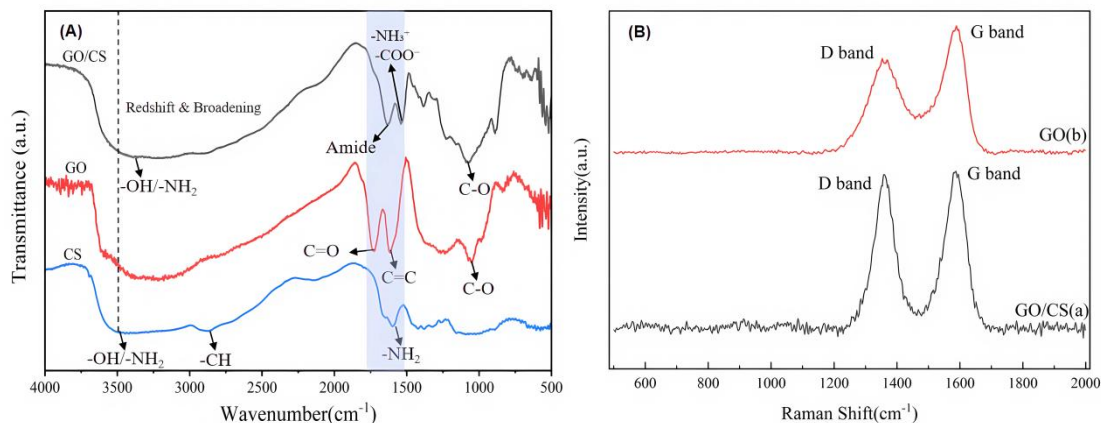


Fig. 2. Interfacial chemical bond reorganization and carbon skeleton defect evolution. (A) FT-IR spectra of (a) GO/CS, (b) GO, and (c) CS, confirming the formation of the multiple crosslinked network; (B) Raman spectra of (a) GO/CS and (b) GO, revealing the increase in topological defects of the carbon skeleton.

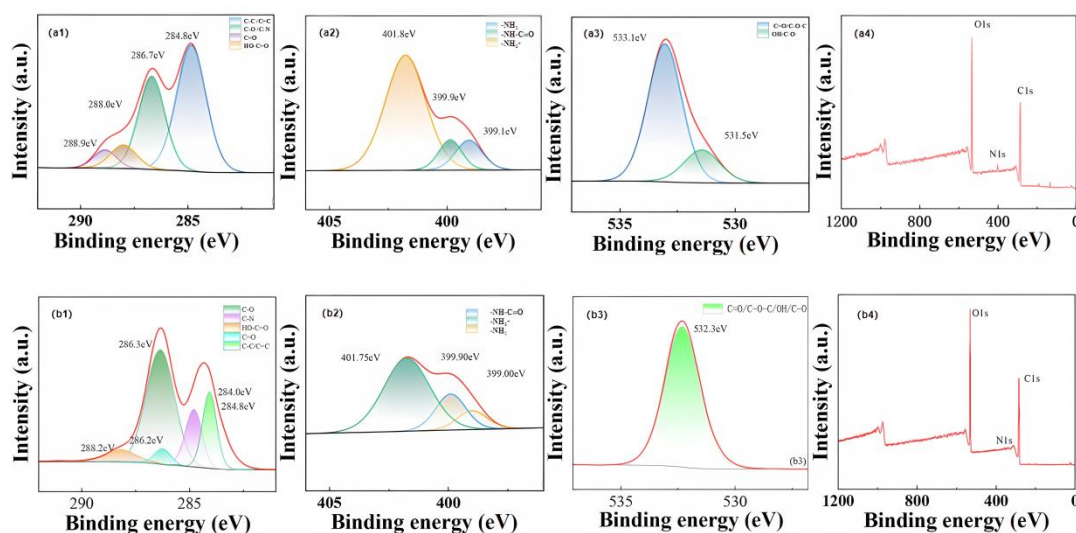
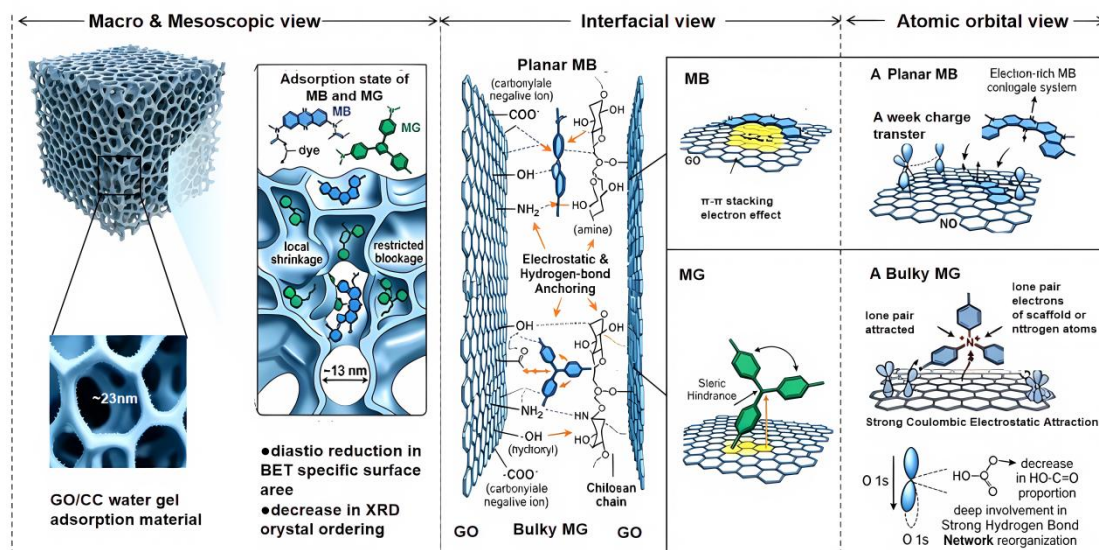


Fig. 3. Spectroscopic quantification of local electronic states and atomic orbitals before and after crosslinking. XPS spectra comparison between (a) pristine GO and (b) GO/CS hydrogel, including high-resolution fitted spectra of C 1s (a1, b1), N 1s (a2, b2), O 1s (a3, b3), and survey spectra (a4, b4).



Scheme 2. Schematic representation of the steric-dependent physico-chemical synergistic adsorption mechanism of the GO/CS double-crosslinked hydrogel.

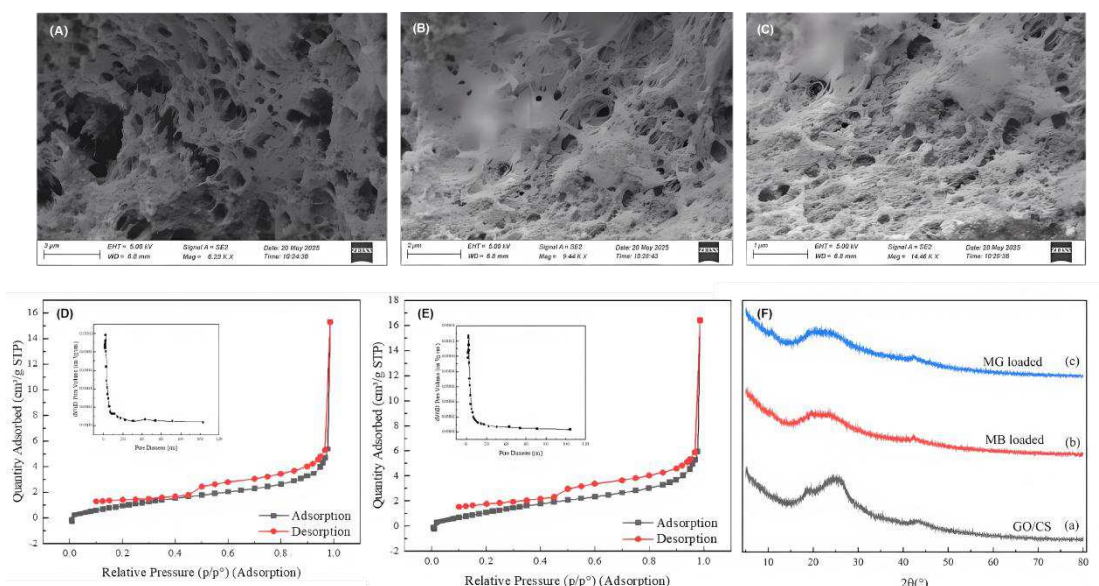


Fig. 4. Micro-interfacial reconstruction and restricted mass transfer behavior induced by dye capture. Morphological evolution: SEM images of (A) pristine GO/CS, and GO/CS after adsorption of (B) MB and (C) MG; Mesoporous network shrinkage characteristics: N₂ adsorption-desorption isotherms of GO/CS after (D) MB and (E) MG adsorption; (F) XRD patterns of (a) pristine GO/CS, and GO/CS after (b) MB and (c) MG adsorption, revealing spatial lattice perturbations caused by macromolecular intercalation.

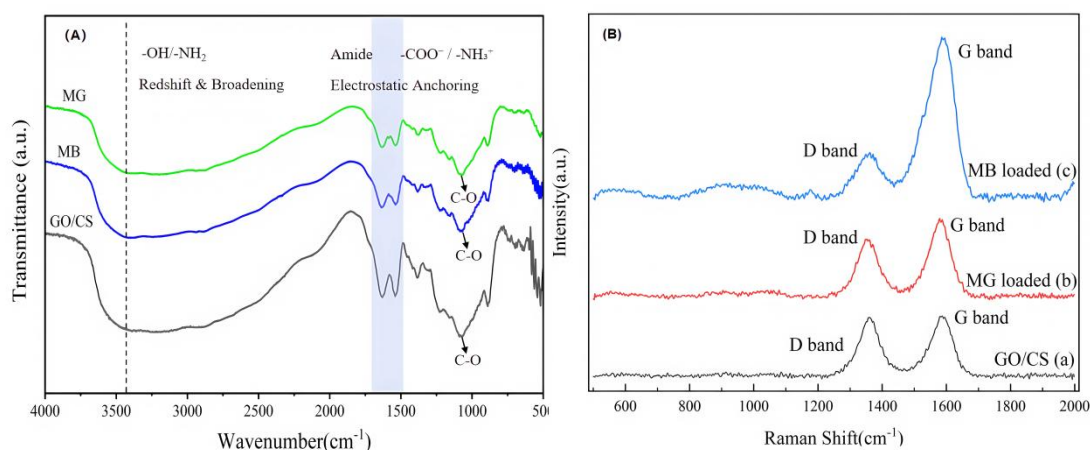


Fig. 5. Optical evidence of multidimensional non-covalent interactions. (A) Comparison of FT-IR spectra: (a) pristine GO/CS and GO/CS after (b) MB and (c) MG adsorption, confirming polar group anchoring responses; (B) Raman spectra revealing the steric-dependent π - π optical shielding effect.

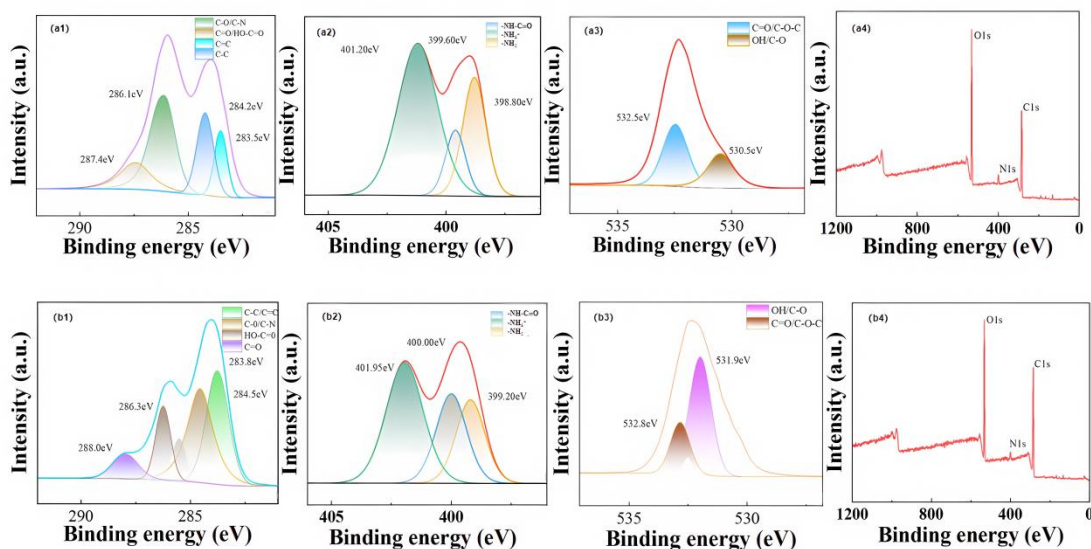


Fig. 6. Charge transfer and electronic state rearrangement during targeted dye interception. XPS high-resolution spectra analysis of GO/CS hydrogel after the adsorption of (a) planar MB and (b) bulky MG. Subfigures correspond to C 1s (a1, b1), N 1s (a2, b2), O 1s (a3, b3), and survey spectra (a4, b4), respectively.

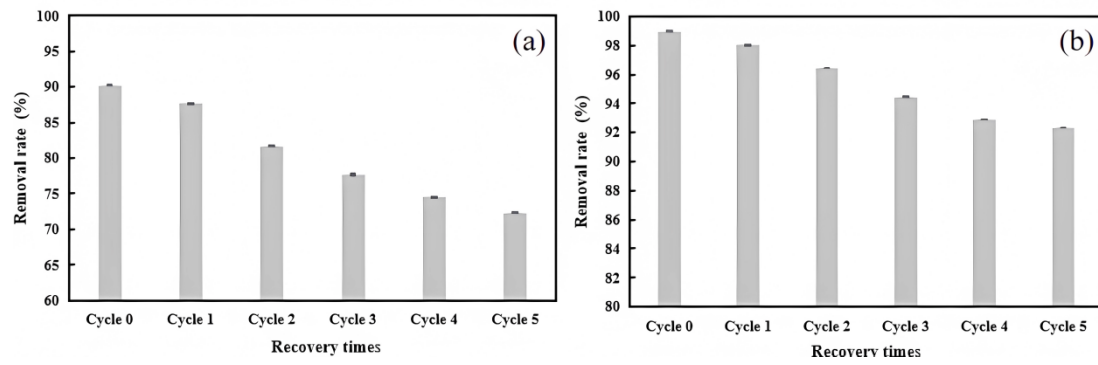


Fig. 7. Long-term regeneration performance and operational stability evaluation of the GO/CS hydrogel towards (A) MB and (B) MG continuous adsorption.

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