

Mechanistic Elucidation on the Detoxification of Hexavalent Chromium Using a Magnetic "Anion Sponge" Fe₃O₄-pC₃N₄/PANI Composite with Redox Capability: Experimental Design and Computational Study

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2.4. Characterization of the adsorbent

The porosity of Fe₃O₄-pCN/PANI was evaluated by N₂ adsorption at -196 °C in a volumetric analyzer (Tristar, Micromeritics, Norcross, GA, USA). Before the experiments, the sample was outgassed at 120 °C for 12 h under vacuum.¹ The specific surface area (S_{BET}), total pore volume (V_{total}), and the micropore volume (V_{MICRO}) were acquired from the gas adsorption data. The Fe₃O₄-pCN/PANI surface features were visualized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS) analysis (SEM, JEOL, JSM-IT200). Raman measurements were performed with a Witec Alpha 300 micro-Raman spectrometer equipped with a 532 nm incident laser light source releasing 5 mW. The point of zero-charge (PZC) of the Fe₃O₄-pCN/PANI sample was investigated by a similar potentiometric titration route reported in our previous work.² Following the addition of 0.03 g of the prepared adsorbent to 50 mL of KNO₃ (0.05 M) solution, the pH of the solution was adjusted from 2 to 12 by adding HCl (0.1 M) or NaOH (0.1 M) aqueous solution. During the 24 h stirring period, the mixtures were kept at an ambient temperature. The final pH_f of each solution was measured. PZC is identified when ΔpH (pH_f – pH_{initial}) is equal zero. A PerkinElmer Nexion 350X inductively coupled plasma-mass spectrometer (ICP-MS) was used to measure total Cr concentrations in the solutions. Prior to analysis, samples were filtered through 0.45 μm filter to remove particulates, acidified with ultrapure HNO₃ (pH < 2) to stabilize dissolved metals, and diluted with deionized water to match the calibration range.

Thermogravimetric and differential thermoanalysis (TGA-DTA) were recorded on the Fe₃O₄-pCN/PANI from 25 to 900 °C using a TA instrument model (STA-1640). The crystal structures of the Fe₃O₄-pCN/PANI hybrid composite were assessed by X-ray powder diffraction (XRD) (BRUKER D8 ADVANCE TWIN diffractometer). X-ray

photoelectron spectroscopy (XPS) measurements of the prepared composite were carried out with an ESCALAB 220 XL spectrometer equipped with a monochromatic Al K α X-ray radiation source at 1486.6 eV. The binding energies were calibrated using the 284.8 eV peak of C 1s.

3.1. Characterization

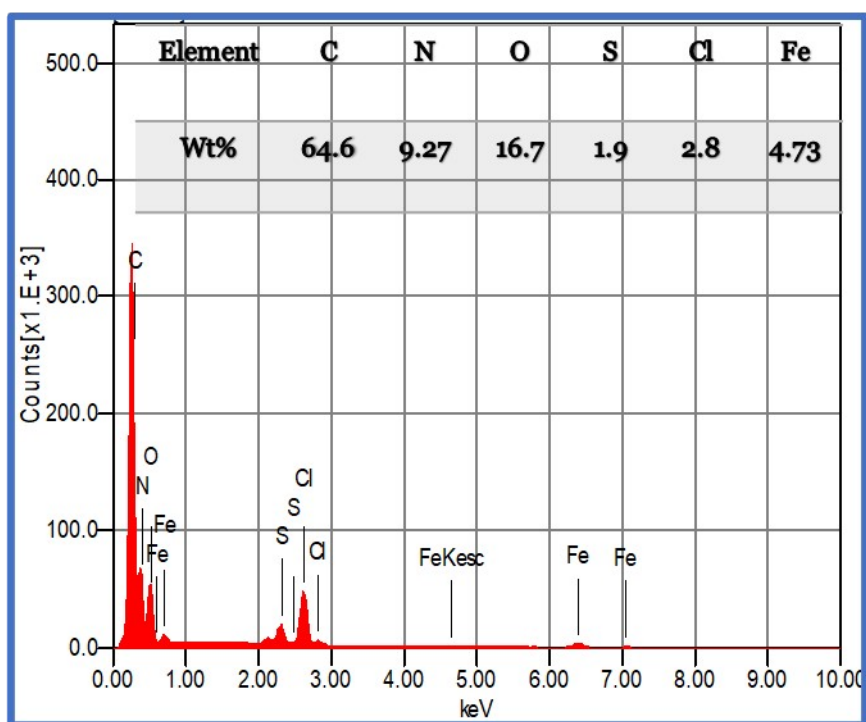
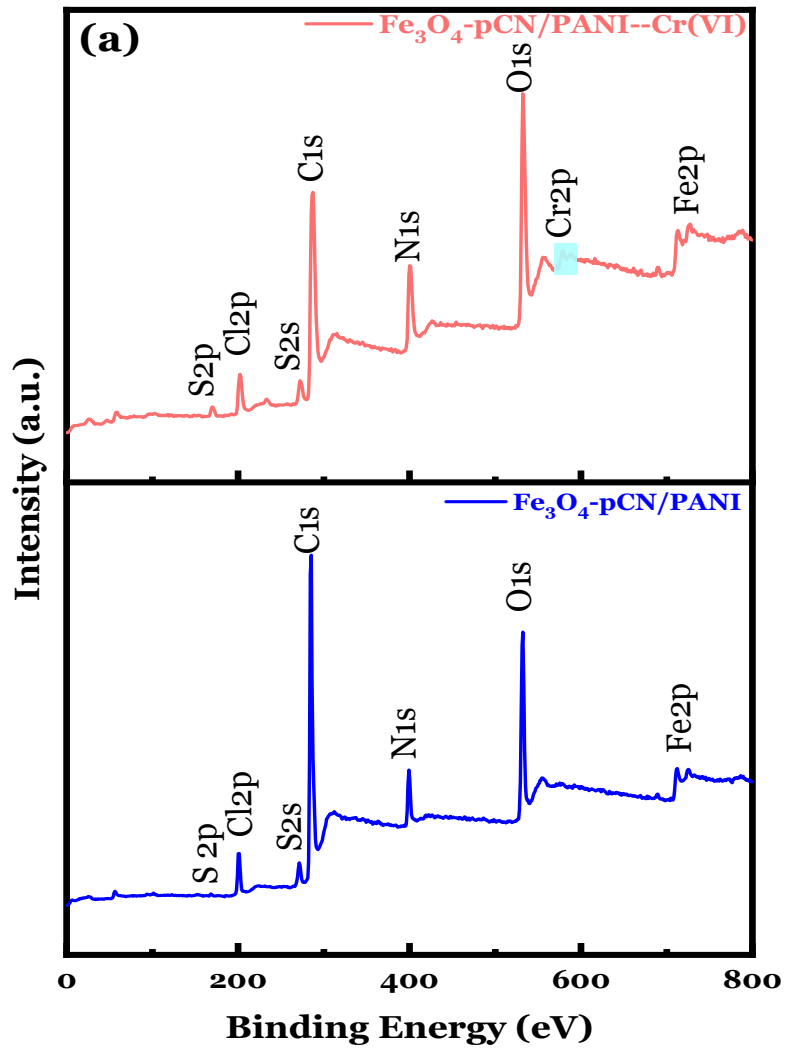


Figure S1. EDS elemental analysis of Fe₃O₄-pCN/PANI.

3.4. Adsorption experiments and probable mechanism – XPS analysis



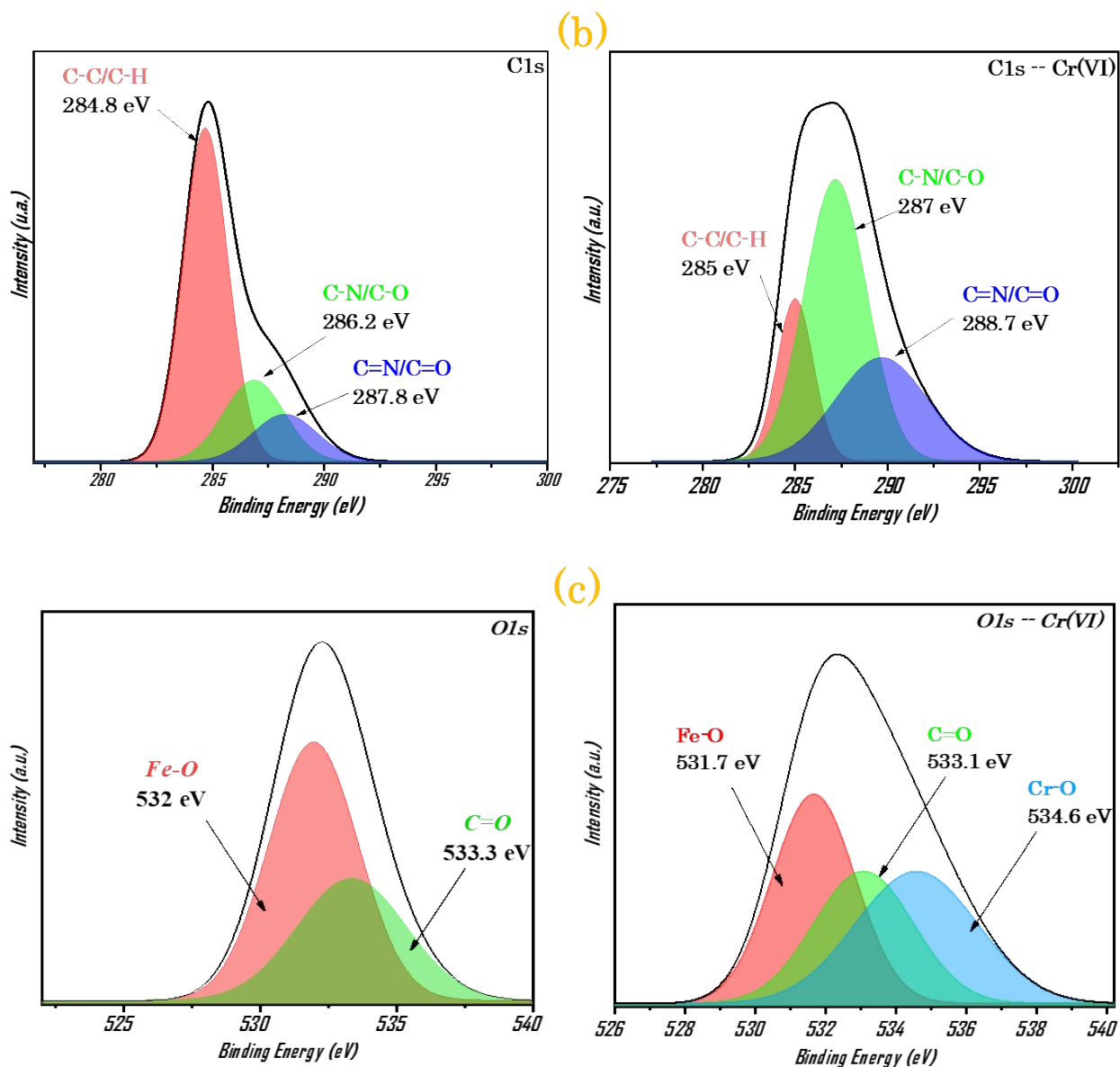


Figure S2. (a) XPS full scans, and high-resolution XPS spectra of (b) C1s and (c) O1s and of the Fe₃O₄-pCN/PANI composite before and after Cr(VI) adsorption.

Table S1: Elemental contents of samples based on XPS survey.

Content (%)	C	O	N	Cl	S	Fe	Cr
Fe ₃ O ₄ - pCN/PANI	49.39	28.96	8.84	7.01	0.62	5.18	-
Fe ₃ O ₄ - pCN/PANI- Cr(VI)	33.56	38.03	13.40	6.63	1.80	3.34	3.24

Table S2: Elemental contents of samples based on XPS survey.

Elements	Deconvolution	Before Cr (VI) removal (%)	After Cr (VI) removal (%)
C 1S	C-C/C-H	70.84	29.73
	C-N/C-O	18.75	51.35
	C=N/C=O	10.41	18.92
O 1S	Fe-O	67.79	43.08
	C=O	32.21	28.37
	Cr-O	-	28.55
N 1S	=N-	25.00	23.38
	N-H	63.16	51.94
	=NH ⁺ -	11.84	24.68
Fe 2p	Fe ²⁺ 2p _{3/2}	45.84	24.81
	Fe ³⁺ 2p _{3/2}	22.28	31.25
	Fe ²⁺ sat	3.26	3.56
	Fe ²⁺ 2p _{1/2}	15.94	17.14
	Fe ³⁺ 2p _{1/2}	7.37	18.51
	Fe ²⁺ sat	5.31	4.73
Cr 2p	Cr ³⁺ 2p _{3/2}	-	41.27
	Cr ⁶⁺ 2p _{3/2}	-	39.68
	Cr ³⁺ 2p _{1/2}	-	7.14
	Cr ⁶⁺ 2p _{1/2}	-	11.91

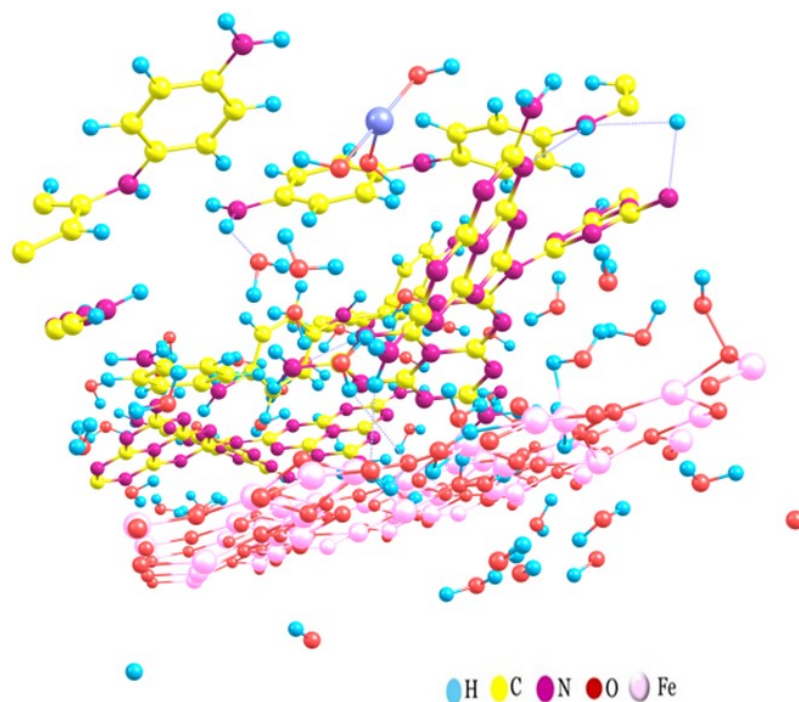


Figure S3. Equilibrium adsorption configurations of Cr(III) mediated by the $\text{Fe}_3\text{O}_4(103)$ -pCN/PANI composite system.

References

- (1) Imgharn, A.; Laabd, M.; Naciri, Y.; Hsini, A.; Mahir, F.-Z.; Zouggari, H.; Albourine, A. Insights into the Performance and Mechanism of PANI@Hydroxapatite-Montmorillonite for Hexavalent Chromium Cr (VI) Detoxification. *Surf. Interfaces* **2023**, *36*, 102568. <https://doi.org/10.1016/j.surfin.2022.102568>.
- (2) Chaoui, A.; Imgharn, A.; Estrada, A. C.; Hamou, A. B.; Farsad, S.; Nouj, N.; Ezzahery, M.; Trindade, T.; Albourine, A.; Alem, N. E. Chromium (VI) Remediation via Biochar@polyaniline Composite: Advancing Water Treatment Using Biogas Residue Digestate. *Adv. Compos. Hybrid Mater.* **2025**, *8* (4), 312. <https://doi.org/10.1007/s42114-025-01345-7>.