



A nitrogen-rich pyridine–melamine porous network for integrated CO₂ capture and hexavalent chromium remediation

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ABSTRACT

Multifunctional adsorbents that integrate greenhouse gas capture with hazardous metal remediation are rare because simultaneously optimizing pore architecture and reactive adsorption sites remains challenging. Herein, a nitrogen-rich pyridine-based poly-melamine porous network (Py-PMAN) was synthesized via Schiff base polycondensation for integrated CO₂ capture and Cr⁶⁺ remediation. The as-prepared polymer combines accessible porosity (S_{BET} of 511.76 m²/g) with reactive amino-pyridine sites that additionally enable oxyanion sequestration. Benefiting from its nitrogen-rich porous structure and abundant amino functionalities, Py-PMAN showed a high CO₂ uptake capacity of 153.03 mg/g at 273 K and 1 bar. Distinct from conventional high-capacity Cr⁶⁺ adsorbents that rely predominantly on electrostatic uptake, Py-PMAN couples adsorption with reduction-immobilization within a porous polymer network. Optimum conditions for Cr⁶⁺ uptake were determined to be pH 3 and a dosage of 0.11 g/L using response surface methodology. Adsorption equilibrium and kinetics were well fitted by the Langmuir isotherm and the pseudo-second-order models, respectively, suggesting monolayer chemisorption and a high Cr⁶⁺ adsorption capacity of 188.68 mg/g. Thermodynamic studies revealed a spontaneous adsorption process. Py-PMAN maintained high Cr⁶⁺ removal efficiency across five adsorption-desorption cycles, indicating excellent reusability and structural stability, while competitive ion experiments confirmed strong selectivity for Cr⁶⁺. FT-IR and XPS analyses revealed that Cr⁶⁺ removal proceeds through synergistic proton-assisted electrostatic binding, reduction-coupled immobilization, and coordination to amino-rich sites, with adsorption governed by these mechanisms. This work presents a robust, multifunctional porous organic network for integrated carbon capture and hazardous-metal remediation, offering a promising strategy for coupled gas purification and wastewater treatment.

1. Introduction

Currently, fossil fuels maintain a predominant position in the global energy system [1–4]. Nonetheless, the combustion of fossil fuels emits significant quantities of greenhouse gases, including carbon dioxide (CO₂) and carbon monoxide (CO) [5,6]. CO₂ is regarded as the principal greenhouse gas, and its substantial emissions have caused numerous environmental issues, this includes rising sea levels, extreme weather events, and environmental degradation [7]. Consequently, the efficient reduction of CO₂ emissions has been an urgent challenge in recent years. The prevailing technique employing an aqueous ethanolamine solution as the absorbent for CO₂ capture is among the most widely used methodologies in industry [8–11]. Nonetheless, challenges such as elevated

decomposition rates, complex recycling processes, and wastewater treatment have constrained its further advancement [12].

Water contamination is a prevalent environmental issue that significantly endangers human health and sustainable development [13–16]. In recent years, large quantities of heavy metals have been released into the environment, posing a serious threat to human health and the normal growth of other species [17–19]. Chromium (Cr) is one of the most hazardous heavy metals present in water, occurring primarily as Cr³⁺ and Cr⁶⁺, with Cr⁶⁺ exhibiting toxicity 100 times greater than that of Cr³⁺ [20]. Chromium is primarily produced through industrial processes such as chromite extraction, the textile and leather industries, electroplating, steel manufacturing, rubber fabrication, and dye production [19–23]. Cr⁶⁺ is toxic to humans, animals, and plants, and can

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induce cancer, teratogenic effects, genetic mutations, and various other health issues [21]. Currently, various technologies are employed for Cr^{6+} removal, including electrolysis [22], ion exchange [23], electrochemistry [24], photocatalytic degradation [25], membrane filtration [26], biological treatment [27], and adsorption [28]. Among these methods, adsorption has garnered significant attention as a viable technique for the removal of Cr^{6+} owing to its cost-effectiveness, simplicity, speed, and high efficiency [29].

Polymeric materials have garnered heightened interest as adsorbents for Cr^{6+} or CO_2 owing to their extensive surface area, distinctive porosity, good selectivity, and high adsorption capacity [30–32]. Among polymeric materials, those containing amine and imine groups, which can interact with metals, have been extensively used as adsorbents for the extraction of heavy metals from wastewater and other contaminated aqueous solutions [33–35]. In 2009, Schwab et al. [36] synthesized an additional polymer by condensing aromatic aldehydes with melamine (MA) at 180 °C, using dimethyl sulfoxide (DMSO) as the solvent. It is noteworthy that secondary amines, rather than imines, extensively cross-link the polymer frameworks. This phenomenon occurs because the resulting imines undergo an additional nucleophilic attack by the MA-specific amine groups ($-\text{NH}_2$), allowing one molecule of carbonyl aldehyde to participate in a condensation reaction with two molecules of ($-\text{NH}_2$). Secondly, the resultant amines serve as cross-linking bridges within the polymers. MA is regarded as the knitting agent, and the resulting polymers are referred to as MA-knitted polymers. Subsequently, several polymers were reported as MA knitted in DMSO and are widely used as adsorbents for capturing CO_2 and removing heavy metals [2]. For example, three triphenylamine-derived polyaminal networks (TMPs) are successfully synthesized via the direct polycondensation of triphenylamine-based aldehydes with MA, achieving a CO_2 uptake that reached 15.7 wt% (273 K) and 11.2 wt% (298 K) at 1 bar [37]. Sandín et al. [33] were successful in fabricating a novel polyaminal network that displayed a high specific surface area (424 m^2/g) and demonstrated adsorption capacity of 27.22 mg/g for Cr^{6+} . Recently, three aromatic ketones were used as monomers to undergo a condensation reaction with MA in DMSO, resulting in the successful preparation of three MA-knitted polymers by Zhang et al. [2]. The resulting polymers demonstrated superior CO_2 adsorption and Hg^{2+} removal, achieving a CO_2 capacity of 171 mg/g at 273 K and 1.0 bar and a Hg^{2+} capacity of 702 mg/g at 298 K. Additionally, the polymeric materials exhibited potential applications for removing several contaminants from water. For instance, Rashidi et al. [38] synthesized a cysteine-functionalized gold nanoparticle/covalent organic framework composite (Cys-AuNPs@COF) for efficient Cr^{6+} removal from water. The material exhibited a maximum adsorption capacity of 151.5 mg/g under optimal conditions: pH 2.5, initial Cr^{6+} concentration of 7.5 mg/L, adsorbent dosage of 0.075 g/L, and a contact period of 7 min. Ibrahim et al. [39] reported a novel polyaminal-linked polymer (PAN-NA) as an effective adsorbent for the removal of various heavy metal ions from aqueous solutions. The material showed selective adsorption of Pb^{2+} , Cr^{3+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , and Ba^{2+} , with adsorption capacities of 90.36, 72.35, 52.79, 24.80, 24.25, and 23.35 mg/g, respectively, at pH 6 and an adsorbent dosage of 20 mg. Furthermore, Almalki et al. [40] reported AgNPs@POPs that showed a high removal efficiency of 99.04% for Cu^{2+} within 20 min at pH 7 and an initial metal-ion concentration of 20 mg/L. Moreover, porous networks with high nitrogen content exhibit substantial adsorption and complexation capacities for Cr^{6+} and facilitate the reduction of Cr^{6+} to Cr^{3+} by providing electrons [41,42].

Recent porous organic polymers have focused primarily on maximizing either CO_2 uptake or the removal of aqueous contaminants in isolation. The multifunctional porous materials have emerged for coupled catalytic or sensing applications; integrated adsorbents for simultaneous gas capture and toxic oxyanion remediation remain largely unexplored.

Therefore, the novelty of this work lies in developing a novel pyridine-based poly melamine network (Py-PMAN), by a Schiff base

polycondensation reaction of acetylpyridine (Py) as a ketone with MA in a DMSO system, which integrates microporous CO_2 capture and redox-active Cr^{6+} sequestration from wastewater within one nitrogen-rich framework, addressing an underexplored multifunctional separation strategy. The chemical structure, surface area, pore size distribution, thermal stability, microporous structures, and surface morphology of the Py-PMAN were investigated using Fourier Transform Infrared Spectroscopy (FT-IR), solid-state ^{13}C Nuclear Magnetic Resonance (ss-NMR), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), X-ray diffractometer (XRD), thermogravimetric analysis (TGA), and Scanning Electron Microscopy (SEM). Utilizing response surface methodology (RSM), the independent variables affecting the batch removal process of Cr^{6+} , including pH and adsorbent dosage, were optimized. The effects of time, initial Cr^{6+} concentration, and temperature on the adsorption process were examined, and the effects of coexisting ions on adsorption and the reusability of the composites after numerous adsorption-regeneration cycles were evaluated. Finally, the adsorption mechanism was proposed through a comprehensive analysis of structural and surface features using scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS), FT-IR, XRD, and XPS of Py-PMAN-Cr.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and reagents used were of high purity (> 99%) and used as received. Detailed information on the materials used in the experiment is provided in the Supplementary Information (S1.1).

2.2. Synthesis of pyridine-based polymelamine network (Py-PMAN)

A flask containing 50 mL of DMSO, in which 1 mmol (0.1122 mL) of acetylpyridine and 8 mmol (1.0008 g) of melamine were dissolved, was heated to 160 °C under a nitrogen atmosphere for 72 h [2]. Following the reaction at room temperature, the solid product was isolated by filtration and subsequently washed sequentially with methanol and deionized water. The product underwent additional purification in a Soxhlet extractor using a water-methanol solution for 12 h. After 24 h of drying at 120 °C, Py-PMAN was obtained as a white powder. A control network sample was synthesized under the same reaction conditions using only MA and DMSO, without 2-acetylpyridine, further to elucidate the role of pyridine units in polymerization, as presented in the Supplementary Information (section S2).

2.3. Characterization

The characteristic properties of the synthesized polymer have been studied using several analytical techniques. Section S1.3 of the Supplementary Information details the specifications of the characterization instruments used in the experiments.

2.4. Assessment of CO_2 capture efficacy

The CO_2 isotherms of Py-PMAN were analyzed using the Micromeritics ASAP 2020 surface area and porosity analyzer at 273 and 298 K, with relative pressure varying from 0.02 to 1 bar. The Clausius–Clapeyron equation was employed to determine the isosteric heat of adsorption (Q_{st}) of CO_2 on Py-PMAN. The Q_{st} were calculated from the isotherms at 273 K and 298 K using the Clausius–Clapeyron eq. (Eq. (1)) [2]. Detailed information regarding the CO_2 uptake experiment is presented in Supplementary Information (section S1.4).

$$Q_{st} = \frac{RT_1T_2\ln(P_1/P_2)}{T_2 - T_1} \quad (1)$$

where R is the Gas constant ($R = 8.314 \text{ J/(K.mol)}$), T_1 and T_2 are the adsorption temperature, P_1 and P_2 represent equilibrium pressure (P/P_0).

2.5. Adsorption experiments of Cr^{6+}

Batch studies were conducted to assess the influence of key independent factors, including pH, dosage, contact time, and temperature on the adsorption process of Cr^{6+} . Optimization research for the Cr^{6+} removal was conducted using RSM with a Box-Behnken Design (BBD). The removal efficiency and adsorption capacity were calculated using the equations Eq. (2) and Eq. (3) [14,43].

$$R (\%) = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

$$Q_e (\text{mg/g}) = \frac{(C_0 - C_e) \times V_L}{m_g} \quad (3)$$

where C_0 and C_e are the concentrations of Cr^{6+} before and after adsorption, respectively. V_L and m_g are the volume of solution containing adsorbate in liters, and the weight of the adsorbent in grams. The kinetic study, adsorption isotherms, and thermodynamic parameters were conducted to define the optimum contact time, estimate the maximum adsorption capacity, and evaluate the spontaneity of the adsorption process, respectively. The potential efficacy of the Py-PMAN adsorbent was examined in various water samples, as well as the effect of coexisting ions was demonstrated. Also, the evaluation of the adsorbent was extended, and reusability tests were conducted across five adsorption-desorption cycles. Detailed information was presented in the Supplementary File (S1.5-S1.9).

3. Results and discussion

3.1. Synthesis and characterization of Py-PMAN

The porous polymer network (Py-PMAN) was prepared through Schiff base polycondensation reaction in DMSO, as depicted in Fig. 1. DMSO is a good solvent characterized by high polarity and a high boiling point; it can break down into thioalcohol and formaldehyde at elevated temperatures, such as 150°C [44]. The released formaldehyde can undergo an in-situ condensation reaction with MA to produce melamine-formaldehyde resin [34,45]. Consequently, it is suggested that formaldehyde is created incrementally in this reaction, initially reacting with MA to generate a polymelamine network intermediate [46]. Additionally, 1 mol of formaldehyde can react with 2 mol of $(-\text{NH}_2)$ of MA to produce secondary amines, leaving behind a large amount of $(-\text{NH}_2)$. Significantly, these persist as $(-\text{NH}_2)$ groups, which are distanced from one another, thereby significantly reducing steric hindrance. Acetylpyridine can subsequently integrate into the polymer chains and undergo a Schiff base reaction with the residual $(-\text{NH}_2)$ of the intermediates, resulting in the formation of imines. The suspended $(-\text{NH}_2)$ groups of the intermediate can be regarded as the cross-linking

bridges for the synthesis of Py-PMAN, as seen in the Supplementary Information (Fig. S1).

The structure of Py-PMAN was examined using FT-IR, solid-state ^{13}C NMR, XPS, SEM, XRD, TGA, and BET analysis. The FT-IR spectra in Fig. 2a demonstrated that the extensive adsorption band at 3365 cm^{-1} was attributed to the secondary amine ($\text{N}-\text{H}$). Furthermore, the presence of imine bond ($-\text{N}=\text{C}-$) at 1654 cm^{-1} corroborates the Schiff base interaction of acetylpyridine with the $(-\text{NH}_2)$ group of the intermediate polymer [46]. The characteristic ($\text{C}=\text{N}$) stretching of the triazine ring in the range $1463\text{--}1541 \text{ cm}^{-1}$ was present after the condensation reaction, and the peak at 1346 cm^{-1} corresponded to the ($\text{C}-\text{N}$) stretching. This suggests that MA was successfully incorporated into the polymers [47]. Notably, there is a diminished ($\text{C}=\text{O}$) stretching with an enhanced ($\text{N}-\text{H}$) stretching, likely due to the interaction of several residual amino groups with the ($\text{C}=\text{O}$) of the ketone, resulting in the attenuation of the ($\text{C}=\text{O}$) stretching [8]. An intense band was seen in the spectra of the Py-PMAN at 1186 cm^{-1} , attributed to the $\text{C}=\text{C}$ stretching of the pyridine ring skeleton [33]. There is a band at 815 cm^{-1} , ascribed to the symmetric $\text{C}-\text{N}-\text{C}$ stretching [39]. Moreover, the FT-IR spectrum of PMAN (Fig. S2a) shows a more intense band at 3371 cm^{-1} , assigned to $\text{N}-\text{H}$ stretching, compared with that of Py-PMAN. This observation indicates that the $(-\text{NH}_2)$ groups of MA may be redundant in this reaction system [2]. Also, the absence of the $\text{C}=\text{N}$ stretching band in PMAN confirms the formation of amination linkages ($-\text{NH}-\text{CH}-\text{NH}-$) [33].

Fig. S2b shows the solid-state ^{13}C NMR spectrum of PMAN; the peak at 166.51 ppm is assigned to the triazine ring carbons, while the absorbance in the range $49.50\text{--}54.78 \text{ ppm}$ is attributed to the methylene carbon ($\text{C}-\text{H}$) in the amination linkage. The collective spectroscopic properties confirm the successful formation of the polymelamine network (PMAN). Additionally, Fig. 2b showed that Py-PMAN had a comparable carbon distribution; however, the carbon signal in the range $49.50\text{--}54.78 \text{ ppm}$ was significantly stronger than in PMAN, indicating a substantial presence of methylene cross-linking bridges in Py-PMAN [2,46,48]. A shoulder peak was observed at the edge of the triazine ring carbon, with a resonance at 156.47 ppm . This peak is likely derived from the Schiff base reaction between the acetylpyridine and the $(-\text{NH}_2)$ group of the PMAN [2]. Furthermore, the two weak signals at around 144.52 and 125.30 ppm can be attributed to the carbons in the pyridine units [37,49]. An additional signal at 13.06 ppm corresponds to the carbon of the methyl group (CH_3) [50]. The XPS examination additionally validates the chemical composition and elemental states of Py-PMAN, as illustrated in Fig. 3. The XPS survey spectrum (Fig. 3a) reveals that Py-PMAN comprises C, N, and O. Fig. 3b shows that the C 1s spectrum of Py-PMAN exhibits four distinct peaks, with binding energies of 284.11 eV , 285.71 eV , 286.76 eV , and 288.41 eV , corresponding to the $\text{C}=\text{C}/\text{C}-\text{C}/\text{C}-\text{H}$, $\text{C}-\text{N}$, $\text{C}=\text{N}$, and $\text{C}-\text{OH}$ configurations, respectively [31]. The $\text{C}=\text{C}/\text{C}-\text{C}/\text{C}-\text{H}$ arrangement originated from the heterocyclic ring; and the $\text{C}-\text{N}$ configuration may correspond to the condensation of MA with formaldehyde [2], whereas the $\text{C}=\text{N}$ is attributed to the carbon of the triazine ring and the pyridine ring. The $\text{C}-\text{OH}$ structure is formed by the condensation of MA and formaldehyde [34,50]. In the N 1s spectrum of Py-PMAN, the three peaks at 398.19 eV , 399.29 eV , and 403.93 eV correspond to the $\text{C}=\text{N}$, $\text{C}-\text{N}$, and $\text{N}-\text{H}$ groups, respectively,

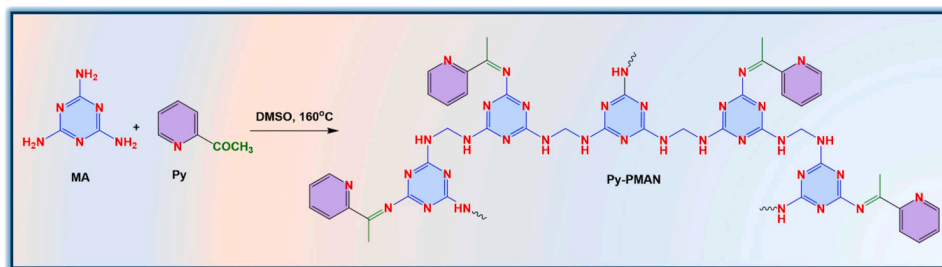


Fig. 1. Synthetic procedure of the aromatic ketone-based polymelamine network in the DMSO system.

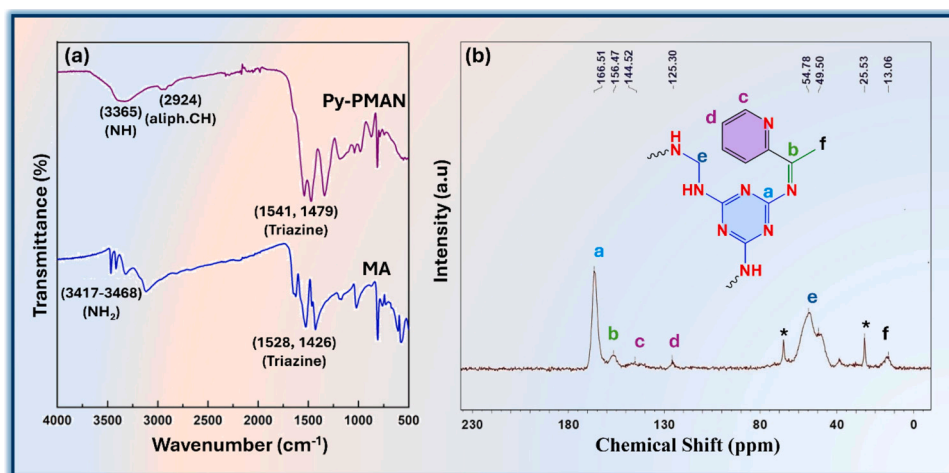


Fig. 2. (a) FT-IR spectra of MA and Py-PMAN, (b) Solid-state ¹³C NMR spectra of Py-PMAN.

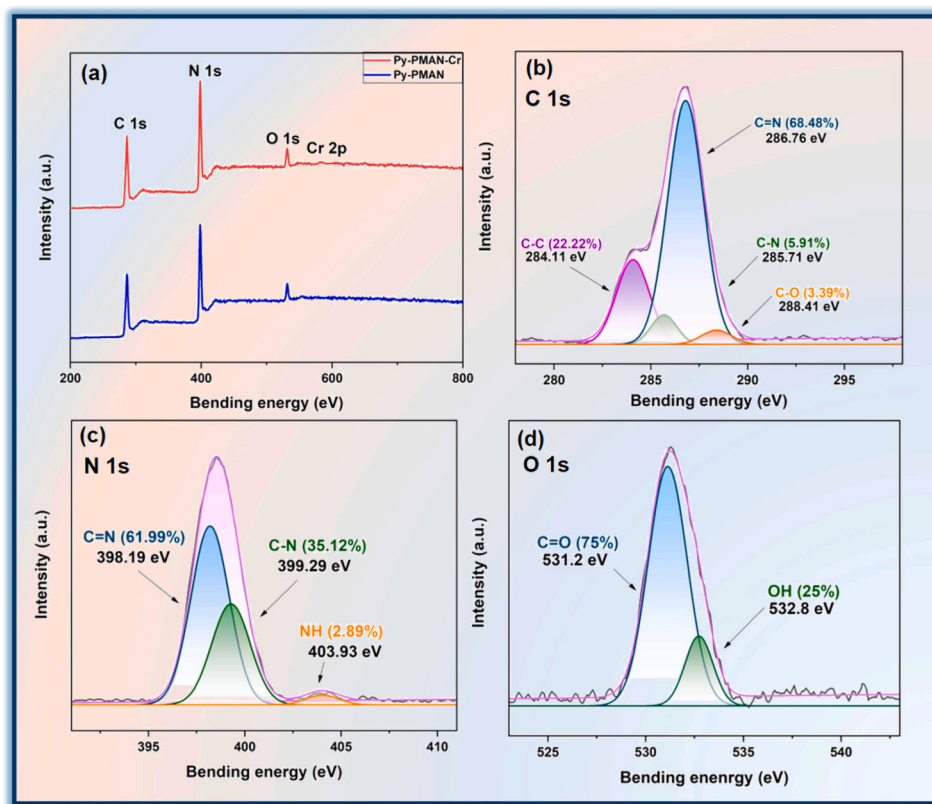


Fig. 3. XPS spectrum of Py-PMAN (a) survey, (b) C 1s, (c) N 1s, and (d) O 1s.

as shown in Fig. 3c. Fig. 3d illustrates the weak peak O1s configuration of the Py-PMAN, where the two peaks at binding energies of 531.2 eV and 532.8 eV may be attributed to the (C—O) and OH, respectively [34]. Based on these findings, it can be concluded that the synthesized Py-PMAN network possesses a high density of functional groups, which significantly enhances its performance in CO₂ adsorption and Cr⁺⁶ removal.

The morphology of the examined PMAN and Py-PMAN was assessed using SEM images. Fig. S3a and Fig. 4a display that PMAN and Py-PMAN have irregular morphology as indicated by the SEM images, as well as noted in other documented melamine-based porous polymers [33]. Following adsorption, the chromium ions permeate the pores, consequently modifying the Py-PMAN structure to a smooth surface (Fig. 4b).

Related to the EDS spectrum (Figs. 4c and S4a), the elemental analysis of the Py-PMAN before Cr⁶⁺ adsorption is displayed, indicating peaks associated with carbon (C), nitrogen (N), and oxygen (O). Figs. 4d and S4b illustrate elemental analysis subsequent to Cr⁶⁺ adsorption, revealing prominent chromium peaks at 0.48 keV and 5.5 keV, thereby affirming the efficiency of Py-PMAN in removing chromium ions. Additionally, the particle diameter in the morphology of Py-PMAN was found to be 34 ± 8 nm, as shown in the TEM image (Fig. S3b).

The thermal stability of Py-PMAN was examined using thermogravimetric analysis (TGA). Measurements were conducted in a nitrogen atmosphere with an average heating rate of 10 °C/min, reaching a temperature of 800 °C. The TGA curve in Fig. S5a indicates that Py-PMAN exhibits exceptional thermal stability at 300 °C. XRD data are

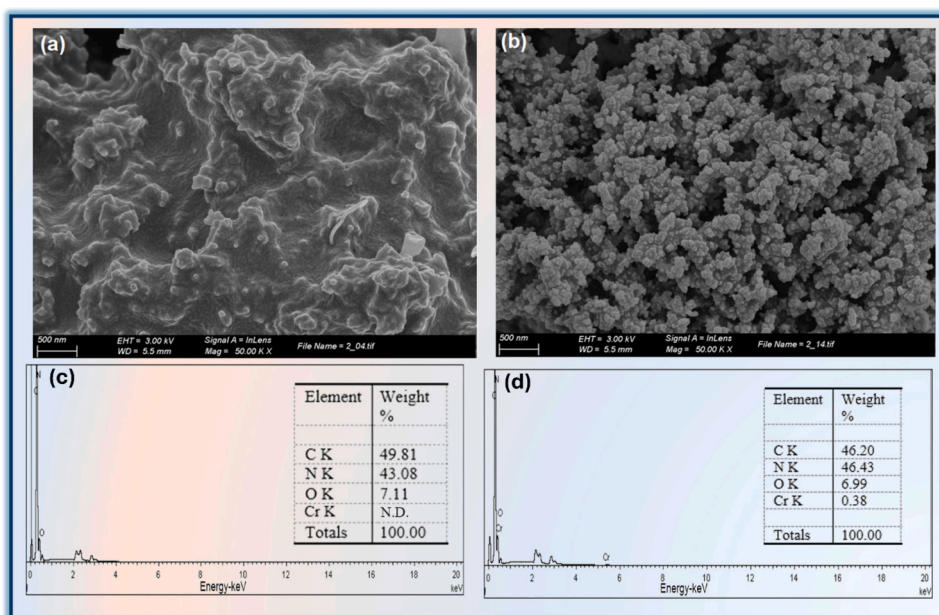


Fig. 4. SEM images of (a) Py-PMAN, and (b) Py-PMAN-Cr; EDS spectra of (c) Py-PMAN and (d) Py-PMAN-Cr.

presented in Fig. S5b. Py-PMAN exhibits large diffraction peaks at $10\text{--}30^\circ$, indicating its amorphous nature as a polymer [31]. After adsorption, the distinctive XRD peak of the Py-PMAN adsorbent exhibits minor shifts from 20.79° to 20.32° . This minor modification is ascribed to the adsorption of chromium. The porosity characteristics of the Py-PMAN were analyzed using nitrogen sorption studies performed at 77 K. Fig. 5a illustrates that the Py-PMAN exhibits isotherms of type II profile according to the IUPAC classification [51]. This type, characterized by the N_2 sorption isotherm of the synthesized polymeric network, exhibits evident gas absorption at low pressure ($P/P_0 < 0.01$), which confirms that Py-PMAN has a microporous structure. Subsequently, in the intermediate pressure range, virtually horizontal adsorption occurs. Moreover, when the relative pressure increases to $P/P_0 > 0.8$, nitrogen uptake increases significantly, suggesting the existence of larger mesopores mostly attributed to interparticle voids resulting from the loose aggregation of tiny particles, as illustrated by SEM micrographs [39,52]. The pore size distribution of Py-PMAN, as illustrated by the nonlocal density functional theory (NLDFT) technique in Fig. 5b, reveals the distribution of micropores and mesopores. The predominant micropore size is 1.47 nm, while the principal mesopores are organized from 2.62 to 6.67 nm.

The information in Table S1 demonstrates the porosity of the

polymeric network, where the Langmuir surface area (S_{Langmuir}) and the BET surface area (S_{BET}) are determined to be 684.98 and $511.76 \text{ m}^2/\text{g}$, respectively, with a micropore surface area (S_{micro}) of $327.42 \text{ m}^2/\text{g}$. The micropore contribution ratio to the overall specific surface area ratio ($S_{\text{micro}}/S_{\text{BET}}$) is 0.63, indicating that Py-PMAN is classified as a microporous polymer [39]. The micropore volume and total pore volume of Py-PMAN are $0.15 \text{ cm}^3/\text{g}$ and $0.57 \text{ cm}^3/\text{g}$, respectively. Thus, a confirmation of the contribution of the pyridine units in the polymerization process and in the formation of the porous Py-PMAN was demonstrated by comparing with the lower value of S_{BET} for the intermediate network (PMAN) ($102 \text{ m}^2/\text{g}$) [2].

3.2. CO_2 capture

Porous materials containing N atoms inside their structures exhibit a remarkable capacity to interact with CO_2 molecules, hence boosting CO_2 uptake [31,50]. The synthesized Py-PMAN in the present work exhibits substantial nitrogen content and an extensive surface area, facilitating its evaluation for CO_2 collection applications. The CO_2 adsorption of Py-PMAN was assessed up to 1 bar at 273 and 298 K, with the resulting isotherms illustrated in Fig. 6a. At 273 K, the maximum CO_2 absorption recorded was 153.03 mg/g (15.30 wt%), which represents one of the

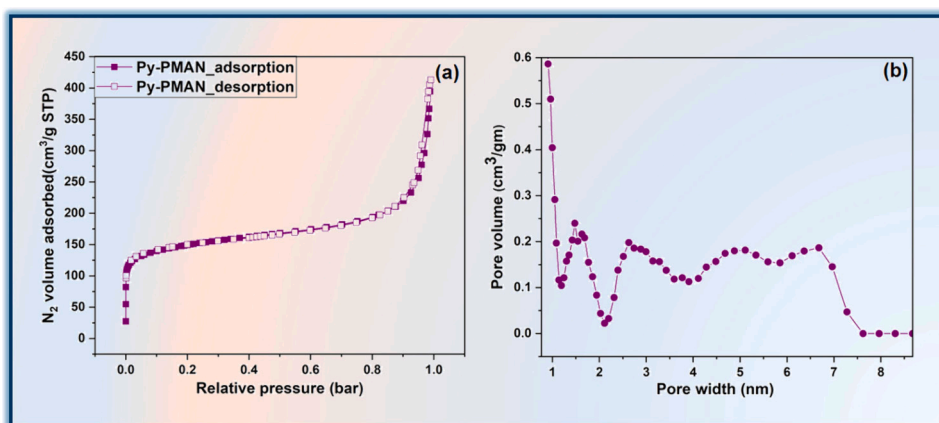


Fig. 5. (a) N_2 adsorption-desorption isotherms of Py-PMAN, (b) pore size distribution of Py-PMAN.

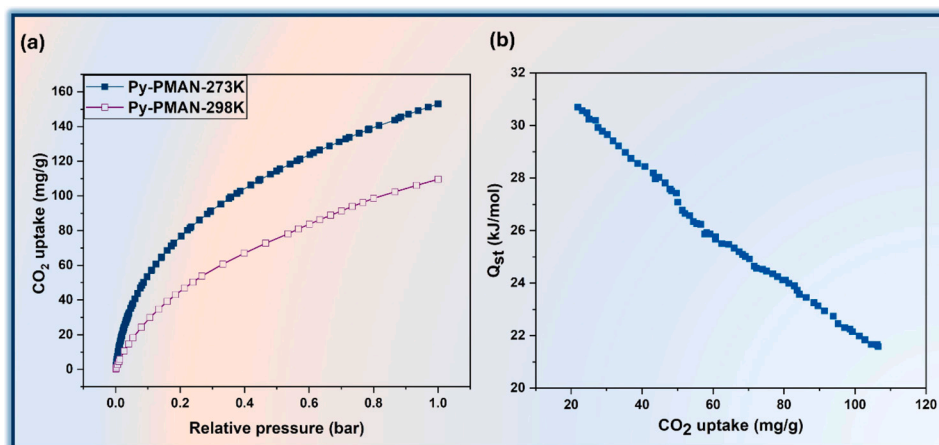


Fig. 6. (a) CO₂ captured in the pores of Py-PMAN at 273 and 298 K, (b) Isothermic heat (Q_{st}) adsorption plot of CO₂ adsorption for Py-PMAN.

most significant uptakes documented for porous polymers under comparable conditions (Table 1). Also, this value confirms that the pyridine rings in the pyridine-containing polymer (Py-PMAN) enhance CO₂ capture compared with the control polymelamine network that reported a value of 55 mg/g under the same conditions (273 K and 1.0 bar) [2]. Moreover, at 298 K, the material exhibited a CO₂ absorption of 109.64 mg/g (10.96 wt%), which is encouraging compared with values reported for other porous materials with different surface areas. This may be due to the high nitrogen content of the MA-based polymers, which is advantageous for CO₂ sequestration. Gaussian 09 W software (version 9.5) was utilized to simulate the electrostatic potential (ESP) distribution of Py-PMAN, thereby illustrating the activity of high-density nitrogen active sites. Fig. S6 illustrates the presence of a positive electric field at the triazine nitrogen sites and pyridine nitrogen sites, which function as favorable adsorption locations. Furthermore, the CO₂ adsorption capabilities of the synthesized material increased with rising relative pressure and decreased with increasing adsorption temperature. This demonstrated that Py-PMAN displayed high interaction with CO₂ molecules, and its CO₂ capture was an exothermic process [31]. To elucidate the precise interaction between CO₂ and the synthesized polymer, the Q_{st} was computed from the isotherms at 273 K and 298 K (Fig. 6b) in accordance with the Clusius-Clapeyron equation [53]. The Q_{st} ranged from 21.58 to 30.69 kJ/mol, suggesting that CO₂ was physically adsorbed on Py-PMAN (<40 kJ/mol) rather than through chemisorption [54]. To further assess the separation potential of the synthesized Py-PMAN porous polymer, the CO₂/N₂ selectivity was estimated from the single-component adsorption isotherms using the Henry initial-slope method. The Py-PMAN shows a little N₂ absorption (~4.18 mg/g) in the measured pressure range (Fig. S7). The CO₂/N₂ selectivity was estimated using the Henry's law initial slope approach by analyzing the low-pressure sections (< 0.3 bar) of the CO₂ and N₂ adsorption isotherms at 273 K (Fig. S8). The CO₂/N₂ selectivity at 273 K was found to be 55.56, which is comparable to values reported for several state-of-

the-art nitrogen-enriched porous polymers at 273 K, including thienyl-based microporous polyaminals (45.8) [55], melamine-based porous polyamides (9.5–35.1) [8], and a hyper-cross-linked polymer (HCP-TPB) (16–42) [56], while offering the advantage of enhanced mass transfer kinetics due to the mesoporous structure. The enhanced performance could be due to the synergistic effects of the nitrogen-rich framework and pyridine-like moieties. In addition, the (N–H and C=N) groups improve the polarity of the framework and enhance the CO₂ affinity. These features, together with the accessible pore architecture, generate adsorption sites that favor CO₂ over N₂ and thus enhance selectivity. Also, the moderate yet competitive selectivity, combined with mesopores, indicates that surface chemistry, rather than pore confinement, is the dominant factor governing low-pressure CO₂/N₂ discrimination in this system. The result is consistent with the overall behavior of nitrogen-containing porous polymers, in which electron-rich heteroatoms induce greater CO₂ sorption through stronger host–guest interactions.

3.3. Cr⁶⁺ removal

The Cr⁶⁺ adsorption screening experiments were conducted to evaluate the role of pyridine units in the polymeric network at an initial concentration of 10 ppm, an adsorbent dose of 1 g/L, and pH 6. The removal efficiency of Cr⁶⁺ increased from 10% for PMAN to 88.01% for Py-PMAN. Hence, the remaining experiments focused on the Py-PMAN adsorbent for the elimination of Cr⁶⁺, which is significantly influenced by solution pH and dose. Consequently, the adsorption tests were optimized using RSM, followed by a kinetic study to find the optimum contact time. After establishing the optimum conditions for Cr⁶⁺ removal, the synthesized adsorbent was applied to real water matrices, and its properties, including maximum adsorption capacity, are further discussed later.

3.3.1. Optimization of Cr⁶⁺ ion removal using RSM

The experimental design offered critical insights into the effects of different factors on the capture efficiency and sorption capacity of the Py-PMAN system. This study examined the factors of material dosage in grams per liter (g/L) and pH level at 10 mg/L of Cr⁶⁺ initial concentration in 100 mL of solution. Table 2 and Fig. 7 present experimental design, including the independent variables, actual and coded values, as well as the associated removal percentages and adsorption capacities. The results indicated that removal percentages and adsorption capabilities varied under different testing conditions. As shown in Table 2, in rows 1, 4, and 6, where the pH was set at 3, the removal percentages achieved were 96.01%, 75.76%, and 89.54%, respectively. The data indicates that a reduced pH under these conditions resulted in improved

Table 1
CO₂ uptake parameters of various polymers found in the literature.

Materials	S_{BET} (m ² /g)	CO ₂ uptake (mg/g)		Q_{st} kJ/mol	Reference
		273 K	298 K		
PAN-PD-BrOH	153.60	16.64	10.21	56.32	[31]
PAN-PD	70.40	29.15	19.52	55.18	[31]
NAN-2	56	65.6	39.6	31.5	[57]
NUT-10	101	92	78.2	25.10	[58]
Py-TC-MA	357	93	60.8	41.06	[59]
TPA-TMC-MA	492	123	82.5	25.15	[59]
MTPA	481	126	94	30.77	[8]
Py-PMAN	511.76	153.03	109.64	30.69	This work

Table 2

Response Surface Methodology results for Cr^{6+} adsorption by Py-PMAN using two experimental variables (pH and polymer dose).

No.	Coded value		Real value		Removal (%)	Adsorption capacity (mg/g)
	pH	Dose (g/L)	pH	Dose (g/L)		
1	-1	1	3	1	96.01	9.60
2	0	1	6	1	88.01	8.80
3	1	-1	9	0.1	12.98	12.98
4	-1	-1	3	0.1	75.76	75.75
5	0	-1	6	0.1	6.85	6.85
6	-1	0	3	0.55	89.54	16.28
7	0	0	6	0.55	57.18	10.40
8	0	0	6	0.55	65.59	11.93
9	1	0	9	0.55	39.39	7.16
10	1	1	9	1	73.85	7.39
11	0	0	6	0.55	66.32	12.06

removal efficiency. Additionally, the differences in dose in this investigation significantly affect the clearance percentages and adsorption capabilities. Upon comparing rows 1, 4, and 6, the removal capacity decreased from 75.76 to 9.60 mg/g when the dose increased from 0.1 to 1 g/L. In row 4, with a dosage of 0.1 g/L and a pH of 3, the removal percentage and adsorption capacity were 75.76% and 75.75 mg/g, respectively.

The ideal conditions for Cr^{6+} adsorption on the surface of Py-PMAN were established utilizing RSM. The statistical analysis by ANOVA reveals the significant factors affecting the adsorption capacity and Cr^{6+} removal efficiency using the given adsorbent, as tabulated in Table 3. The p -values of 0.0111 for removal efficiency and 0.0432 for adsorption capacity demonstrate that the model is statistically significant.

The results of Cr^{6+} removal using Py-PMAN, obtained from BBD and RSM, are significant, demonstrating that the chosen factors substantially influence the reaction variables, with pH level identified as the most critical factor affecting Cr^{6+} removal efficiency and adsorption capacity. The 3D response surface plots are useful in analyzing both the primary and interaction impacts of the components. Fig. 7a and b illustrate the influence of pH (A) and dosage (B) on the effectiveness of Cr^{6+} removal and its adsorption capacity. As pH decreases, the efficacy of elimination increases, peaking at approximately pH 3.

The rising trend of plots at high pH and high dosage signifies that these conditions lead to diminished adsorption capacity. While the optimum is obtained at low dose levels and low pH values, a significant decrease in adsorption capacity is observed at very high doses, as shown in Fig. 7b. The surface map corroborates the ANOVA analysis, indicating that pH exerts a more significant influence than dosage, particularly at pH 3.

3.3.2. Adsorption kinetics

The impact of removal duration on the adsorption of Cr^{6+} using Py-PMAN was examined under optimal conditions of pH 3, dose 0.1 g/L, and temperature 298 K, with an initial Cr^{6+} concentration of 10 mg/L, over a period of 5 to 1440 min. The results showed that the adsorption capacity increased significantly and reached saturation within 6 h (Fig. S9a). This pattern is characteristic of adsorption processes where the availability of active sites diminishes with time due to clogging. The adsorption kinetics of Py-PMAN were examined to elucidate the fundamental mechanisms and rate-limiting processes driving the adsorption process, utilizing pseudo-first-order, pseudo-second-order, and intra-particle diffusion models [43]. Table 4 presents the adsorption kinetics equations, kinetic parameters, and experimental adsorption capacities for Cr^{6+} removal utilizing Py-PMAN through three kinetic models.

The pseudo-first-order kinetic model showed a correlation with the experimental data (Fig. S9b), as indicated by an R^2 value of 0.9209. Nevertheless, the slope of the Figure concerning the rate constant was relatively minor (-0.0007), indicating that the process is more complex in systems with uneven adsorption. The values of k_1 and Q_e , derived from the slope and interception of the graph are displayed in Table 4.

Table 3

Analysis of variance for the response of the adsorption capacity for Cr^{6+} .

Source	Sum of squares	d _f	Mean square	F-value	P-value	
Removal efficiency (%)						
Model	8144.99	5	1629.00	10.47	0.0111	Significant
A-pH	3042.18	1	3042.18	19.55	0.0069	
B-Dose	4389.41	1	4389.41	28.21	0.0032	
AB	412.52	1	412.52	2.65	0.1644	
A ²	240.71	1	240.71	1.55	0.2687	
B ²	134.88	1	134.88	0.8669	0.3946	
Residual	777.94	5	155.59			Not significant
Lack of fit	726.32	3	242.11	9.38	0.0979	
Pure error	51.62	2	25.81			
Cor total	8922.93	10				
Adsorption capacity (mg/g)						
Model	2644.55	3	881.52	4.65	0.0432	Significant
A-pH	915.58	1	915.58	4.83	0.0640	
B-Dose	811.91	1	811.91	4.28	0.0773	
AB	917.06	1	917.06	4.84	0.0638	
Residual	1327.35	7	189.62	1.55		
Lack of fit	1325.64	5	265.13	310.66	0.0032	
Pure error	1.71	2	0.8534			Significant
Cor total	3971.90	10				

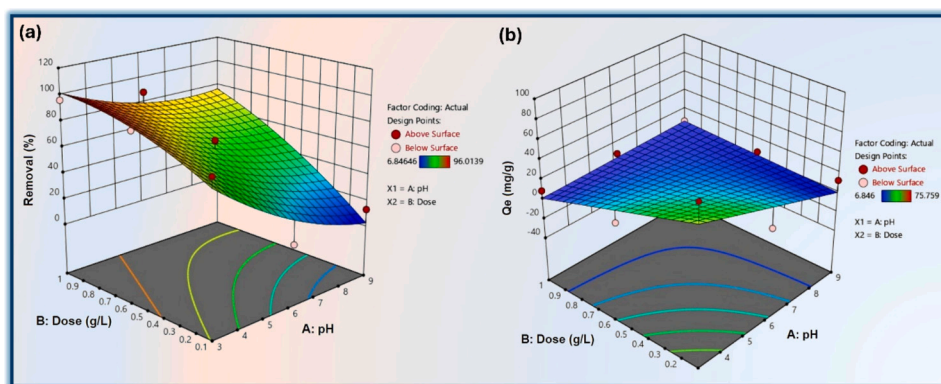


Fig. 7. Response surface plots of: (a) removal efficiency and (b) adsorption capacity versus the effect of two variables (dose and pH).

Table 4Kinetic parameters and experimental adsorption capacities for Cr⁶⁺ onto Py-PMAN.

Kinetic model	Equations	Rate constant	Calculated Q _e (mg/g)	Experimental Q _e (mg/g)	R ²
Pseudo-first order	$\log(Q_e - Qt) = \log(Q_e) - \frac{K_1}{2.303}t$	K ₁ (min ⁻¹) 1.4244	28.11	74.78	0.9209
Pseudo-second order	$\frac{t}{Q_t} = \frac{t}{(K_2 Q_e^2)} + \frac{t}{Q_e}$	K ₂ (g/mg/min) 0.0008	72.46		0.9987
Intra-particle diffusion	$Q_t = (K_{id} t^{1/2}) + Q$	K _{id} (mg/g/min ^{1/2}) 0.7245	43.92		0.9199

Where: Q_e and Q_t (mg/g): the amounts of Cr⁶⁺ adsorbed at equilibrium and at the time (hour), respectively. K₁ (min⁻¹): the first-order adsorption rate constant. K₂ (g/mg/min): the rate constant for pseudo-second-order chemisorption, K_{id}, (mg/g/min^{1/2}): the intra-particle diffusion rate constant.

The computed values and the experimental values of Q_e do not correspond. This is evidenced by the disparity between the values of estimated Q_e and observed Q_{exp}, suggesting that a pseudo-first-order reaction does not accurately represent the sorption of Cr⁶⁺ onto Py-PMAN [60]. Conversely, a pseudo-second-order model (Fig. S9c) exhibited an outstanding fit to the experimental data, as indicated by a remarkably high R² value of 0.9987. The correspondence between the computed and observed Q_e values substantiates the assertion that the pseudo-second order model accurately characterizes the removal process by the Py-PMAN sorbent. This indicates that the pseudo-second-order model effectively characterizes the rapid adsorption rate of Cr⁶⁺ onto Py-PMAN, but the pseudo-first-order model is unsuitable [61].

Additional insight into the diffusion mechanism can be derived from the intra-particle diffusion model (Fig. S9d). The intra-particle diffusion model elucidates the movement of metal ions from the fluid layer surrounding the adsorbent surface to the internal adsorption sites via pores, which govern the diffusion rate. The pronounced concentration gradient between the film and the solid surface facilitates rapid solute transport into the surface [43]. The R² value of 0.9199, although lower than that of the pseudo-second-order model, suggests that inter-particle diffusion is involved but does not constitute a rate-limiting factor [62].

3.3.3. Adsorption isotherms

Isotherm analysis is the most suitable method for designing and evaluating the efficacy of the sorption process. Analyzing experimental equilibrium data provided significant insights into the process. Models such as Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) are employed to evaluate adsorption equilibrium data. We evaluated the adsorption isotherms of Py-PMAN over a range of initial Cr⁶⁺ concentrations (5–200 mg/L) at pH 3 and 298 K, using 2 mg of Py-PMAN. Fig. S10a illustrates the variation in the adsorption capacity of Py-PMAN, which ranged from 34.10 to 209.15 mg/g, in relation to Cr⁶⁺ concentration, spanning from 5 to 200 mg/L. As Cr⁶⁺ concentration rises, adsorption capacity rises as well, although the rate of growth slows at higher concentrations. This indicates that the polymeric material has a good ability to remove Cr⁶⁺ over a wide concentration range, but at the higher end of the range it begins to approach equilibrium. The observed trend is attributed to the saturation of adsorption sites and diffusion restrictions within the polymeric network. At low initial Cr⁶⁺ concentrations, a large fraction of surface sites on Py-PMAN remains unoccupied, and the driving force for adsorption (i.e., the concentration gradient between the bulk solution and the solid–liquid interface) is significant. Consequently, these readily available sites interact efficiently with Cr⁶⁺ ions, resulting in a rapid initial increase in adsorption capacity. As the Cr⁶⁺ concentration increases, the available active sites become progressively occupied. As the number of unoccupied sites diminishes and the system approaches saturation, the rate of adsorption decreases. In this regime, the adsorption capacity increases only slowly with concentration, reflecting the approach to equilibrium. This behavior is consistent with Langmuir-type adsorption, where a finite number of homogeneous sites leads to a maximum adsorption capacity at high concentrations. The reduced adsorption rate at higher Cr⁶⁺ concentrations may also be attributed to slower diffusion of the solute into the polymer's inner pores. After the initial rapid adsorption phase,

in which surface sites are readily accessible, the adsorption process becomes increasingly limited by the diffusion of Cr⁶⁺ ions into the adsorbent interior as external surface sites are occupied. The combined effect of these factors can thus explain the observed pattern: a rapid rise in adsorption capacity at lower Cr⁶⁺ concentrations due to abundant unoccupied sites and a strong driving force, followed by a gradual approach to equilibrium as the active sites of Py-PMAN become saturated and pore diffusion becomes rate-limiting at higher concentrations. Moreover, the fitting results and correlation coefficients for the elimination of Cr⁶⁺ using the synthesized material under three isotherm models are presented in Fig. S10 and Table 5. The results indicate that the Langmuir adsorption model exhibits a superior correlation coefficient (R² = 0.9965) compared to the Freundlich model, (R² = 0.7089). The elevated R² value indicates that the adsorption of Cr⁶⁺ onto Py-PMAN occurs in a homogeneous system with analogous constrained regions, consistent with monolayer adsorption [20].

A crucial component of the Langmuir isotherm is the separation factor (R_L = 1/(1 + K_LC₀)), which can be utilized to ascertain whether the adsorption process is advantageous. In this context, K_L denotes the Langmuir adsorption isotherm constant, whereas C₀ (mg/L) signifies the concentration of the adsorbate in the initial solution before the adsorption process. The value of R_L can indicate the adsorption tendency: irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1), or unfavorable (R_L > 1) [63]. Moreover, a smaller R_L indicates a stronger affinity between the adsorbent and the adsorbate [64]. Based on the equation presented in Table 5, the computed value of R_L was 0.5, suggesting that the adsorption reaction was favorable and that the affinity between the adsorbent and adsorbate was substantial. The D-R isotherm was employed to ascertain the nature of sorption, distinguishing between physical and chemical sorption on both homogeneous and heterogeneous surfaces [65].

3.3.4. Thermodynamic study

Thermodynamic studies were conducted to determine the feasibility of Cr⁶⁺ adsorption onto Py-PMAN at temperatures ranging from 298 to 318 K. The experimental dataset was analyzed using the Van't Hoff model and presented in Fig. S11 and Table 6. The thermodynamic

Table 5Adsorption isotherms equations and constants for the adsorption of Cr⁶⁺ onto Py-PMAN.

Isotherm models	Equations	Constants	R ²
Langmuir	$\frac{C_e}{Q_e} = \frac{1}{(K_L Q_{max})} + \frac{C_e}{Q_{max}}$	Q _{max} (mg/g) 188.68	K _L (L/mg) 0.688
Freundlich	$\log Q_e = \log K_f + \frac{1}{n} \log C_e$	K _F (mg.L/g) 52.42	n 3.16
DR	$\ln Q_e = \ln Q_s - \beta \epsilon^2$	Q _s (mg/g) 0.010	E (kJ/mol) 12.91

$$\epsilon = RT \ln \left[1 + \frac{1}{C_e} \right]; C_e \text{ (M)}, R = 8.314 \text{ J/mol.K, and } T = 298 \text{ K.}$$

parameters of adsorption, ΔG° , ΔH° , and ΔS° , were calculated by equations in the supplementary information file (section S1.6). The uniformly negative ΔG° values at all examined temperatures (-8.291 , -6.818 and -4.088 kJ/mol for 298, 308 and 318 K, respectively), indicated the favorable and spontaneous character of adsorption, demonstrating a strong affinity for Cr^{6+} onto Py-PMAN. The significant negative ΔH° (66.589 kJ/mol) demonstrates its exothermic nature. The negative ΔS° value indicated strong specific interactions (chemisorption, inner-sphere complexation, formation of surface complexes) that often produce negative entropy, because binding to well-defined sites constrains orientation and motion more severely [66].

3.3.5. Assessment of Cr^{6+} removal from diverse water sources using Py-PMAN

The efficacy of the synthesized Py-PMAN adsorbent for Cr^{6+} removal from Milli-Q water, tap water, and wastewater was evaluated by the spiking method. Spike experiments were performed using an adsorbent dosage of 0.11 g/L, a pH of 3, and a contact duration of 6 h as the obtained optimum conditions, and 10 mg/L of Cr^{6+} . The wastewater samples were obtained at multiple process points of the municipal wastewater treatment plant (WWTP) in Martorell (Barcelona, Spain): WWTP inlet (coded as W1), the inlet wastewater to the biological reactor (coded as W2), and the sludge inlet to the centrifuge unit (coded as W3). The elimination percentages of spiked Cr^{6+} samples in Milli-Q water, tap water, W1, W2 and W3 were found to be 74.95%, 72.98%, 57.68%, 70.98%, and 73.18%, respectively. The reduced removal efficiency of Cr^{6+} ions in tap water and wastewater compared to Milli-Q water can be attributed to matrix effects. The presence of competing ions dissolved organic matter, and other background constituents in real water matrices may interfere with adsorption sites or influence the speciation and mobility of Cr^{6+} , thereby decreasing overall removal performance. Nevertheless, the results indicate that Py-PMAN remains effective at removing Cr^{6+} from various water sources, demonstrating its applicability for treating complex, realistic aqueous systems.

3.3.6. Regeneration and reusability studies

For efficient pollutant removal in large-scale industrial applications, the regeneration of adsorbents is essential, as it enables repeated cycles and lower costs. Careful selection of the desorbing agent was essential to guarantee the successful desorption of contaminants [67]. This work evaluated the adsorption efficacy of Py-PMAN toward different water samples through five adsorption-desorption cycles utilizing 0.01 M HNO_3 as the desorption solution (Fig. 8a). The reusability tests were performed utilizing Py-PMAN, and spiked Milli-Q water, tap water and wastewater (W1, W2, and W3) were treated with 10 mg/L of Cr^{6+} ions under the previously discussed optimal conditions of pH, dosage, temperature, and contact time.

In the case of spiked Milli-Q water and tap water, the adsorbent exhibits a minor reduction in its removal efficiency across five cycles, decreasing from 74.95% to 60.51% and from 72.98% to 58.51%, respectively. For the wastewater source, after the initial adsorption-desorption cycle, the Cr^{6+} removal efficiency was 52.93%, 54.36%, and 70.91% for W1, W2, and W3, respectively. After that, it decreased to 46.96%, 44.65%, and 60.8% following the subsequent four-adsorption-desorption treatments for W1, W2, and W3 wastewater, respectively. The decline in removal efficacy for Milli-Q water may be attributed to the following; potential obstruction of certain pores inside the adsorbent during the adsorption-desorption process; and the complex established

between the functional groups and Cr^{6+} cannot be desorbed, thus diminishing the quantity of active sites on the adsorbent's surface [61]. Also, the reduction in removal effectiveness for the other water sources may be ascribed to certain active sites on the adsorbent being occupied by Cr^{6+} ions or other analytes from the aqueous matrices that could not be entirely desorbed [15]. Consequently, the recyclability tests indicate Py-PMAN serves as a cost-effective and efficient adsorbent for the extraction of Cr^{6+} ions from different water sources.

3.3.7. Effects of coexisting ions

The synthesized adsorbent, Py-PMAN, was evaluated for its efficacy in adsorbing and removing Cr^{6+} contaminants from aqueous solutions in the presence of other ions. In practical applications, selectivity is essential for adsorbents in the presence of other metal ions. Therefore, the selectivity tests were divided into three parts: 1) the presence of other heavy metals, 2) the presence of other cations, and 3) the effect of anions. We investigated the potential effects of additional heavy metal ions that may be present in water. Consequently, an aqueous solution containing three heavy metal ions (Cr^{6+} , Pb^{2+} , and Cd^{2+}) at an initial concentration of 10 mg/L for each ion was utilized to examine the adsorption selectivity of Py-PMAN for Cr^{6+} under an adsorbent dose of 1 g/L and pH of 6, as well as the presence of a binary mixture and individual heavy metals. The Py-PMAN demonstrated a significantly greater capacity for Cr^{6+} capture, achieving a removal efficiency of up to 75.75%, exceeding other heavy metal ions (28.15% for Cd^{2+} and 15.86% for Pb^{2+}). Thus, this study demonstrated superior efficacy in eliminating heavy metals in anionic forms (Cr^{6+} as $\text{Cr}_2\text{O}_7^{2-}$ or HCrO_4^-) compared to cationic forms (Pb^{2+} or Cd^{2+}) [14,68,69]. Moreover, the presence of Pb^{2+} or Cd^{2+} with Cr^{6+} resulted in a decrease in the Cr^{6+} removal efficiency of 49.62% and 49.63% for Pb^{2+} and Cd^{2+} , respectively. Additionally, a sharp decrease in Cr^{6+} removal efficiency (36.97%) occurs in the presence of three heavy metals. This could be attributed to competition for adsorption at the active site of Py-PMAN. However, interesting results were obtained when the adsorption experiments were carried out at the optimum pH for Cr^{6+} (pH 3) and dose of 1 g/L, where the removal efficiencies were found to be 96.01%, 97.74%, 95.29%, and 95.64% in the case of the absence of other heavy metal ions, presence of Pb^{2+} , presence of Cd^{2+} , and presence of Pb^{2+} and Cd^{2+} , respectively. The results could be attributed to a positive charge that enhances the interaction between the chromium, which is present in anionic form, and to a decrease in interactions with the other heavy metals (Pb^{2+} and Cd^{2+}) due to repulsive forces. Therefore, the Py-PMAN demonstrated a strong selectivity for Cr^{6+} removal. Also, we carefully illustrated the impact of coexisting ionic species on the removal of Cr^{6+} by Py-PMAN in Fig. 8b. In the case of cations (Ca^{2+} and Mg^{2+}) and anions (Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-}), an aqueous solution consists of Cr^{6+} (initial concentration of 10 mg/L) mixed with each cation and anion individually to test the Cr^{6+} selectivity using the synthesized adsorbent. The presence of cations, such as Ca^{2+} and Mg^{2+} , in the solution had the same effect on Cr^{6+} removal by Py-PMAN. For instance, the removal efficiency of Cr^{6+} at pH 6 in the presence of Ca^{2+} or Mg^{2+} was 45.22% and 45.52%, respectively, compared to 75.75% in the absence of other metal cations. Additionally, pH was a critical parameter for Cr^{6+} removal efficiency in an acidic medium (pH 3), where the presence of other cationic metals did not significantly decrease Cr^{6+} removal efficiency (94.67%) compared to the control one that showed a removal of 96.01%. Unlike cations, anions exerted a greater influence on Cr^{6+} adsorption. For instance, the presence of Cl^- , SO_4^{2-} , NO_3^- , or PO_4^{3-} significantly diminished the removal efficacy, demonstrating a substantial effect. The adsorption efficiencies of Cr^{6+} in the presence of PO_4^{3-} , NO_3^- , Cl^- , or SO_4^{2-} were 53.59%, 52.70%, 46.23%, and 18.31%, respectively. From these results, we can see that the remediation efficiency remained consistent across the anions, decreasing only to 18.31% with SO_4^{2-} . This decrease may be attributed to the divalent nature of SO_4^{2-} , which facilitates competitive adsorption with dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) at surface binding sites, thereby significantly reducing the

Table 6
Adsorption thermodynamic parameters for Cr^{6+} removal using Py-PMAN.

Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)	R^2
298	-8.291	-66.589	-0.194	0.9644
308	-6.818			
318	-4.088			

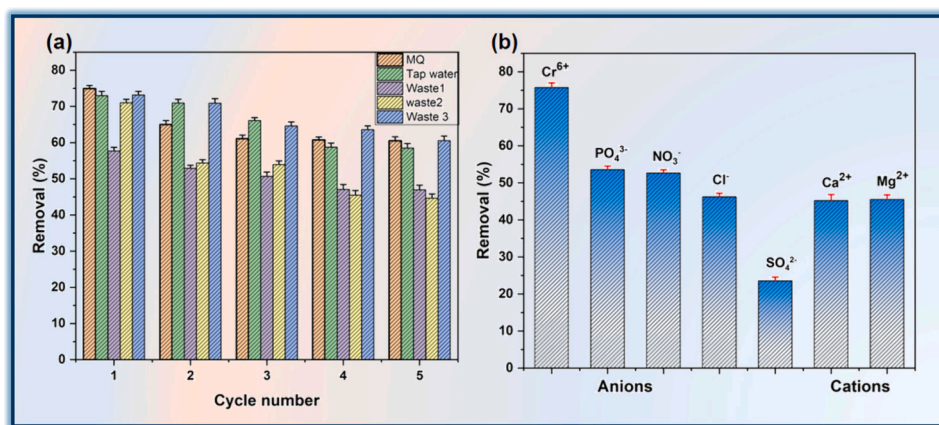


Fig. 8. (a) Removal efficiency for adsorption-desorption cycles on Cr^{6+} and (b) Effect of interfering ions on Cr^{6+} adsorption (Cl^- , SO_4^{2-} , Ca^{2+} , and Mg^{2+} = 100 mg/L, NO_3^- and PO_4^{3-} = 50 mg/L).

efficacy of Cr^{6+} removal via ligand-displacement processes [70].

3.3.8. Performance comparison of Py-PMAN with different adsorbents

This section compares the efficacy of several adsorbents in removing Cr^{6+} from water. The synthesized adsorbent Py-PMAN has a maximum adsorption capability for Cr^{6+} of 188.68 mg/g. The findings of this work unequivocally demonstrate that Py-PMAN possesses a substantial adsorption capacity (mg/g) for the elimination of Cr^{6+} , with the amount of adsorbent used either lower or comparable to that of other documented adsorbents. Additionally, it may be utilized for five adsorption-desorption cycles. In conclusion, the Py-PMAN adsorbent offers a promising option for the effective removal of Cr^{6+} ions from aqueous solutions, owing to its high adsorption capacity, low adsorbent dosage, and short equilibrium time. Compared with reported nitrogen-rich porous adsorbents, Py-PMAN combines competitive CO_2 uptake, selective Cr^{6+} sequestration, and dual-function process capability within a single platform (Table 7).

3.3.9. Adsorption mechanism

By studying adsorption kinetics, adsorption isotherms, and thermodynamic studies, it is demonstrated that the adsorption of Cr^{6+} primarily arises from chemical interactions between the Py-PMAN and the pollutant. The groups on Py-PMAN were compared and evaluated after adsorption using FT-IR spectroscopy to identify the adsorption sites (Fig. S12). It was found that the intensities of the N—H, N=C, C—N—C,

Table 7

Comparison of Cr^{6+} adsorption capacity between Py-PMAN and other reported adsorbents.

Adsorbent	pH	Adsorption capacity (mg/g)	Adsorbent dosage (g/L)	Ref.
L-Cyst- Fe_3O_4 NPs	2	34.50	2	[71]
Polydopamine-decorated SBA-15	3	44.05	—	[72]
HCPs-N	—	44.50	—	[73]
Melamine functionalized SBA-15	3	50.00	4.00	[74]
CS@nZVI-CMC NC	—	96.91	0.1	[14]
CTF500	5	97.84	—	[75]
PCA	3	117	0.4	[76]
Cys-AuNPs@COF	2.5	151.5	0.4	[38]
Hazelnut shell activated carbon	1	170	2.5	[77]
Py-PMAN	3	188.68	0.11	This work
Fe_3O_4 @COF-MT@PPy	2	429.18	0.1	[20]
PU@nZVI	2	600.00	0.5	[43]

and C=C peaks decreased. Moreover, we observe red-shifts at 3375, 1650, 1340, and 1190 cm^{-1} , respectively, indicating that these groups were the main adsorption sites. To support the FT-IR, XPS was employed in this investigation to characterize Py-PMAN after adsorption. The distinctive peaks of C 1s, O 1s, N 1s, and Cr 2p were observed on Py-PMAN, in the overall spectrum depicted in Fig. 3a. Simultaneously, Cr 2p_{3/2} and Cr 2p_{1/2} as depicted in Fig. 9d exhibit pronounced diffraction peaks at 576.8 eV and 585.4 eV, respectively, after adsorption, which indicate the successful adsorption of Cr^{6+} . Additionally, the Cr 2p_{3/2} peak can be deconvoluted into two components, Cr^{6+} and Cr^{3+} , exhibiting energies of 577.8 eV and 575.8 eV, with molar percentages of 64.14% and 35.86%, respectively. The presence of (—NH— and —N=) groups on the surface of Py-PMAN are easy to protonate to (—NH₂⁺ and —NH⁺=) in an acidic medium. The presence of Cr^{6+} may be attributed to the adsorption of Cr^{6+} by electrostatic interactions between these positively charged groups and Cr^{6+} anions. The results indicated that Cr^{6+} was reduced to Cr^{3+} during adsorption, and Cr^{3+} was also adsorbed via chelating interactions. This is attributed to the protonated amine groups on the synthesized material surface undergo a redox reaction with Cr^{6+} to yield Cr^{3+} , which exhibits a significant affinity for amine groups [30]. In the N 1s spectrum after adsorption (Fig. 9b), the energy changes of (C=N) and (C—N) were 0.37 eV and 0.30 eV, respectively. The peak regions of (C=N) decreased by 14.98%, whereas (C—N) increased by 18.67% suggesting that these nitrogen configurations served as the primary adsorption sites for Cr^{6+} . Moreover, Fig. 9a illustrates that with the adsorption of Cr^{6+} by Py-PMAN, the binding energies of (C—C), (C=N), (C—N) and (C—O) in the high-resolution C 1s spectrum shift to 283.90 eV, 286.68 eV, 285.42 eV and 288.33 eV, respectively. Moreover, it was found that the intensity of the peak (C—O) increased by 7.01%, demonstrating that C—O (C—OH and C—O—) bonds immobilized Cr^{6+} via chemical complexation (Fig. 9c). Furthermore, some studies indicate that —OH may interact with Cr^{6+} more through hydrogen bonding [41]. Analysis of the O 1s peak revealed a substantial reduction in the strength of the —OH characteristic peak, up to 23.61%. Moreover, to distinguish between true chromium immobilization and possible reduction to soluble Cr^{3+} , total chromium concentrations in both the filtrate and Cr-loaded solid were measured. Total Cr in the filtrate was determined by oxidizing Cr^{3+} to Cr^{6+} using KMnO_4 before colorimetric determination. The XPS analysis of the chromium-loaded polymer surface revealed the coexistence of both Cr^{6+} and Cr^{3+} species, with Cr^{6+} accounting for 64.14% and Cr^{3+} for 35.86% of the total chromium detected (Fig. 9). This distribution provides critical evidence of the adsorption mechanism and confirms that partial reduction of Cr^{6+} to Cr^{3+} occurs during adsorption. The presence of substantial Cr^{6+} (64.14%) indicates that electrostatic adsorption remains the dominant mechanism, where Cr^{6+} oxyanions (HCrO_4^- and

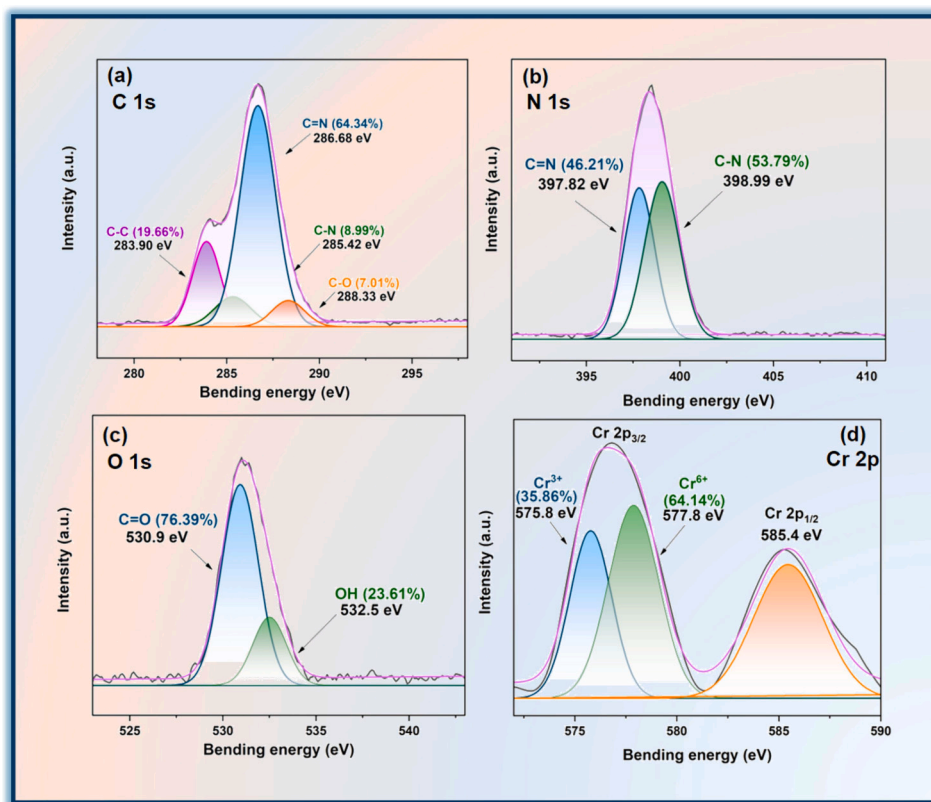


Fig. 9. XPS spectrum of Py-PMAN-Cr (a) C 1s (b) N 1s (c) O 1s and (d) Cr 2p.

CrO_4^{2-}) are attracted to positively charged functional groups on the polymer surface at acidic pH. Simultaneously, the detection of Cr^{3+} (35.86%) suggests that a fraction of the

adsorbed Cr^{6+} undergoes reduction, likely facilitated by electron-donating functional groups (e.g., amine, hydroxyl, or carboxyl groups) present in the polymer matrix. This reduction phenomenon is consistent with previous studies on polymer-based adsorbents, where Cr^{6+} reduction to Cr^{3+} was attributed to the redox-active nature of the adsorbent surface [43]. Also, the 96.01% removal efficiency of Cr^{6+} demonstrates the synthesized polymer's high adsorption capacity under the experimental condition of pH 3 and a dose of 1 g/L. The relatively high removal percentage, coupled with the XPS-determined $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio, suggests a dual-stage adsorption mechanism: (1) initial electrostatic attraction and adsorption of Cr^{6+} oxyanions onto positively charged sites, followed by (2) partial reduction of adsorbed Cr^{6+} to Cr^{3+} , which may subsequently be retained through ion exchange or complexation with functional groups. The fact that Cr^{6+} remains the predominant species on the surface (64.14%) indicates that the reduction process is incomplete, and the adsorbent primarily functions through selective Cr^{6+} uptake rather than through complete reduction. This finding is advantageous for practical applications, as it suggests that the polymer can effectively remove toxic Cr^{6+} from wastewater while minimizing the generation of Cr^{3+} , which, although less toxic, still requires proper management. The observed $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio (64.14:35.86) is also consistent with the pH-dependent adsorption behavior. At the experimental pH of 3.0, the polymer surface is positively charged, promoting Cr^{6+} oxyanion adsorption. However, the acidic environment also favors the reduction of Cr^{6+} to Cr^{3+} by electron transfer from functional groups, resulting in the observed 35.86% Cr^{3+} content. The incomplete reduction (i.e., Cr^{6+} still dominant) suggests that the adsorbent maintains strong affinity for Cr^{6+} , which is critical for selective removal from $\text{Cr}^{3+}/\text{Cr}^{6+}$ mixed systems.

Furthermore, the mass balance between the 96.01% removal

efficiency and the XPS percentages indicates that the adsorbed chromium species are stably retained on the polymer surface, with minimal leaching or desorption during adsorption. The combined XPS and removal data confirm that the synthesized polymer operates via a synergistic adsorption-reduction mechanism, delivering superior performance relative to adsorbents that rely solely on electrostatic interactions. This dual mechanism enhances overall removal capacity and provides a more robust solution for Cr^{6+} remediation in industrial wastewater treatment.

According to these results, the adsorption mechanism of Cr^{6+} on the Py-PMAN adsorbent can be summarized as shown in Fig. 10: the anion Cr^{6+} was adsorbed onto the amine groups on the surface of Py-PMAN through electrostatic interactions. Then, the reduction of part of Cr^{6+} to Cr^{3+} through a redox reaction by the positively charged amines on the Py-PMAN surface occurred, followed by the chelation reaction between Cr^{3+} and NH groups on the adsorbent surface. Finally, hydrogen-bonding interactions between OH groups on the surface and Cr^{6+} took place.

4. Conclusions

A nitrogen-rich pyridine-based poly-melamine porous network (Py-PMAN) was successfully developed through Schiff-base polycondensation as a multifunctional adsorbent for integrated CO_2 capture and Cr^{6+} remediation. The engineered porous framework combines a high surface area and an accessible pore architecture with abundant amino-rich active sites, enabling competitive CO_2 uptake (153.03 mg/g at 273 K and 1 bar) with a favorable Q_{st} value and efficient, selective Cr^{6+} sequestration from wastewater (up to 75% removal because of SO_4^{2-} level in the matrix). Moreover, adsorption studies demonstrated that Cr^{6+} uptake (188.68 mg/g) follows Langmuir monolayer behavior and pseudo-second-order kinetics, while thermodynamic analysis confirmed a spontaneous, exothermic, and chemisorption adsorption

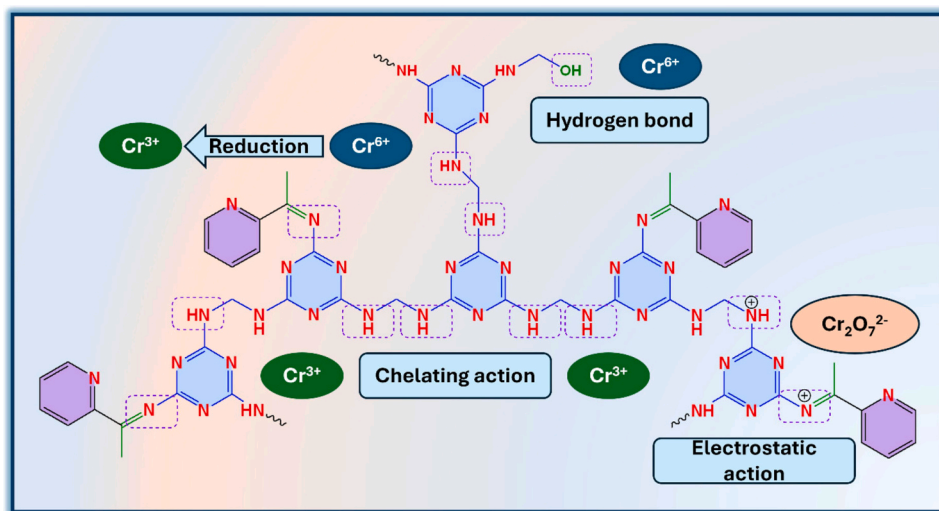


Fig. 10. Proposed mechanism of Cr^{6+} adsorption by Py-PMAN.

process. Spectroscopic investigations revealed that Cr^{6+} removal is governed by synergistic proton-assisted electrostatic attraction, reduction-coupled immobilization, and coordination interactions at nitrogen-containing active sites. Moreover, Py-PMAN maintained excellent regeneration stability over repeated cycles, highlighting its practical durability.

Importantly, beyond demonstrating dual-function performance, this work establishes a structure–function strategy in which microporous adsorption domains for CO_2 capture and reactive adsorption sites for hazardous oxyanion sequestration are integrated within one porous organic network. This coupled-separation concept distinguishes Py-PMAN from conventional single-purpose adsorbents and provides a broader framework for the design of multifunctional adsorbents. IAST calculations and mixed-gas adsorption experiments will be performed in future work to provide a comprehensive evaluation under realistic post-combustion conditions. Also, future work will focus on extending the evaluation of the effectiveness of Py-PMAN for Cr^{6+} removal from rural water matrices, such as rural wastewater, where the influence of competing ions, organic matter, and other matrix components can be systematically assessed. From an engineering perspective, the combined adsorption performance, selectivity, and reusability suggest potential for application in integrated flue gas purification and wastewater treatment processes. More broadly, this work offers a promising pathway toward heteroatom-rich porous materials for coupled environmental separations and sustainable remediation technologies.

CRediT authorship contribution statement

Laila S.A. Ali: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ahmad Abo Markeb:** Writing – review & editing, Software, Methodology, Formal analysis, Conceptualization. **Javier Moral-Vico:** Writing – review & editing, Supervision, Resources. **Adriana Artola:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.179309>.

Data availability

Data will be made available on request.

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