



Enhanced adsorptive removal of chromium (VI) ions from wastewater with phosphorus-doped magnetite-carbon composite: advanced statistical physics modeling and kinetic studies

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Received: 25 December 2024 / Accepted: 18 October 2025
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Abstract

The primary aim of this research was to design a sustainable phosphorus-doped magnetite nanoparticle-embedded activated carbon, synthesized from *Acacia falcata* leaves, for the efficient adsorption of hexavalent chromium (Cr(VI)) from wastewater. The methods involved chemical modification and magnetization to synthesize the adsorbent, followed by characterization using XPS and EDS to confirm elemental composition and the reduction of Cr(VI) to Cr(III). Batch studies were carried out spanning the temperatures from 293 to 323 K, and advanced statistical physics models were utilized to examine the adsorption isotherms. The findings showed that the Two Layer One Energy model exhibited the best correlation with the experimental results (χ^2 : 0.003–1.262, R^2 : 0.997–0.999), with an orientation factor ($n < 0.5$) indicating parallel alignment of Cr(VI) ions on the Af-MAC, enhancing adsorption efficiency. The optimum saturation adsorption capacity was 114.09 mg/g at 303 K, exceeding values reported for comparable materials. Regeneration studies revealed only a slight decline in efficiency over five cycles due to pore blockage and chromium complexation, while cations had minimal effect, and competing anions reduced removal efficiency. The outcomes observed in this research work suggest that the synthesized Af-MAC exhibits exceptional Cr(VI) adsorption, strong reusability, and high adsorption capacity, resulting in a promising material for Cr(VI) removal.

Keywords Advanced statistical physics modeling · Cr (VI) adsorption · P-doped magnetic activated carbon · Cr(VI) removal mechanism · Wastewater treatment

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1 Introduction

Heavy metals pose a significant threat owing to their harmful properties, persistence, and tendency to bio-accumulate among the various pollutants found in wastewater. The hexavalent oxidation state of chromium Cr(VI), is a widely recognized environmental pollutant from diverse industrial sources, including leather tanning, electroplating, and textile manufacturing. Cr(VI) is highly soluble in water, making it a prevalent contaminant in industrial effluents (Deivayanai et al., 2024). The mobility and bioavailability of Cr(VI) in aquatic systems further exacerbate its environmental impact, facilitating its incorporation into the food web and threatening marine ecosystems and humans. The health effects of Cr(VI) are well-documented, with numerous studies highlighting its carcinogenic and toxic properties (Yu et al., 2021). Chronic exposure to Cr(VI) is attributed to an increased likelihood of several cancers, notably lung cancer, and additional health problems, including respiratory disorders, skin ulcers, and kidney damage (Mohanty et al., 2023).

Traditional techniques for Cr(VI) abatement comprise ion exchange, precipitation, and membrane filtration, which face challenges such as elevated operational costs, complex process management, and harmful waste generation (Varnaseri-Ghandali et al., 2024). Chemical precipitation, for example, generates large amounts of sludge, while ion exchange and membrane filtration require frequent replacement of resins and membranes, respectively (Qasem et al., 2021). Among various treatment methods, adsorption has emerged as a preferred option, prized for its straightforward design, high performance, and economic viability. It encompasses the adsorption of contaminants on an adsorbent material, which can then be easily removed from the aqueous solution.

Activated carbon is a highly efficient adsorbent, leveraging its exceptional properties, porous structure, and adaptability in capturing diverse pollutants. Lately, researchers have shown increasing enthusiasm for harnessing affordable biomass materials derived from agricultural waste, plant biomass, and other organic materials as the source of activated carbon (Vinayagam et al., 2023). To produce activated carbon, various chemicals like strong acids, strong bases, and certain salts are typically used, along with high-temperature treatments (Liang et al., 2022). Compared to these chemicals, modification with orthophosphoric acid (OPA) offers benefits such as lower temperature requirements, reduced equipment corrosion, less pollution, and lower costs (Vinayagam et al., 2023).

The biomass was impregnated with OPA and pyrolyzed under an inert atmosphere, where the impregnation step induced significant chemical and physical transformations. Chemically, OPA promotes dehydration and hydrolysis reactions, cleaves glycosidic bonds, partially depolymerizes lignin, and increases carbon yield (Li et al., 2025). It also introduces phosphorus-containing functional groups and enhances oxygenated surface functionalities, thereby improving surface polarity and chemical reactivity (Patra et al., 2020). The presence of OPA during pyrolysis facilitates the removal of volatile matter, suppresses shrinkage, and enhances pore development. These combined effects generate a carbon structure with a higher specific surface area and well-developed porosity compared to carbon obtained by pyrolysis alone.

In addition to acid treatment, the magnetization of activated carbon is an innovative approach to facilitate the easy recovery of the material from treated water (Selvaraj et al., 2022). Magnetization is typically achieved by incorporating magnetic nanoparticles, such as iron oxides, into the activated carbon matrix using the precipitation method. When activated

carbon is magnetized, it retains its enhanced adsorption properties, facilitated by the surface complexation and conversion of Cr(VI) to Cr(III), while also gaining the added benefit of magnetic responsiveness.

In recent years, magnetic activated carbon (MAC) has been extensively studied for the adsorption of various pollutants. Demarchi et al., prepared AC from termite feces using H_2SO_4 and FeCl_3 , followed by carbonization at 600–900 °C to produce MAC. For Cr(VI) removal at 25 °C, the adsorption capacity was 66 mg/g for MAC-800 (Demarchi et al., 2019). Similarly, Ramya et al. synthesized MAC from tannery sludge via a cleaner pyrolysis process at 700 °C (Ramya et al., 2022). The resulting magnetic composite demonstrated a maximum Cr(VI) adsorption capacity of 80.21 mg/g at pH 2.0. Although notable improvements have been reported, adsorbent performance remains far from optimal, underscoring the scope for novel materials and synthesis strategies for MAC. A key advantage of MAC lies in its regenerative potential through chemical and thermal treatments, which augments its reusability, lessens production needs, and minimizes ecological consequences (Juturu et al., 2025).

Acacia falcata leaves are a sustainable and renewable source of activated carbon because of their high carbon composition. Utilizing these leaves aligns with eco-friendly practices and supports efficient adsorption applications for wastewater treatment. In our previous research work, we used these leaves for the synthesis of hematite nanoparticles (Juturu et al., 2024a) and magnetic biochar (Juturu et al., 2024b) and used them for Cr(VI) adsorption. However, magnetic AC prepared from this source, its applications for Cr(VI) removal, and the mechanism analyzed through advanced statistical physics models, remain unexplored, representing a significant research gap.

For adsorption processes, equilibrium data are critical to analyzing the interplay between adsorbate and adsorbent. These data allow researchers to evaluate the adsorption capacity, understand the nature of interactions, and evaluate the optimal conditions for efficient uptake of contaminants. The Langmuir and Freundlich models – the classical isotherms, while commonly employed in adsorption studies, have limitations that statistical physics models can overcome. The Langmuir model assumes monolayer adsorption with uniform sites, neglecting surface heterogeneity and multilayer adsorption, which limits its application to real adsorbents with varied surface characteristics (Messaoudi et al., 2023). The Freundlich model partially accounts for multilayer adsorption and heterogeneity but lacks precision in describing specific site interactions (Sellaoui et al., 2017). Additionally, both models often ignore adsorbate-adsorbate interactions, which can significantly affect adsorption at high surface coverage, and provide limited thermodynamic insights (Xue et al., 2022). In contrast, advanced statistical physics models incorporate multilayer adsorption, variable energy distributions, and adsorbate interactions, allowing them to address heterogeneous surfaces and finite adsorption sites more accurately (Sen & Mondal, 2024). These models offer parameters that link directly to thermodynamic properties, giving a more comprehensive evaluation of adsorption phenomena and improving the predictability and optimization of adsorbent materials.

The objectives of the current study are: (1) to synthesize phosphoric acid-modified MAC from *Acacia falcata* leaves biomass and characterize its physicochemical properties; (2) to evaluate its Cr(VI) adsorption performance under various operational conditions such as dosage, pH, temperature, initial concentration, and time; (3) to analyze adsorption isotherms using advanced statistical physics models, namely One Layer One Energy, Two Layer One

Energy, and Two Layer Two Energy, in order to elucidate the surface interaction mechanisms; (4) to assess the regeneration of the adsorbent; (5) to investigate the effect of competing ions, including sulfate, nitrate, carbonate, and phosphate, on Cr(VI) removal efficiency; and (6) to conduct spiked wastewater studies to evaluate the adsorbent's applicability in realistic water matrices.

2 Materials and methodologies

2.1 Materials

Ferrous sulfate, sodium hydroxide, and 1,5-diphenylcarbazide (DPC) were procured from Merck (India) and used without any further purification. Potassium dichromate, orthophosphoric acid, sulfuric acid, acetone, and hydrochloric acid were supplied by Loba-Chemie Pvt. Ltd. (India). All the reagents and solvents utilized in this study were of analytical grade to ensure the reliability and accuracy of the experimental results, unless otherwise mentioned.

2.2 Synthesis of magnetic activated carbon

A. falcata leaves were collected from the university campus, then washed, air-dried, and pulverized using a mechanical grinder. Next, 5 g *Af* leaves biomass was blended with 10 ml of OPA in a crucible. The contents were dried at 353 K for 10 h to undergo chemical activation. Later, the contents were transferred to a muffle furnace and heated to 673 K for 2 h. The presence of OPA during pyrolysis played a crucial role in promoting dehydration and hydrolysis reactions, which facilitated the breakdown of major biomass constituents such as hemicellulose, cellulose, and lignin. These reactions disrupted the rigid plant polymer network and prevented the formation of tar by stabilizing carbon structures. Additionally, phosphoric acid acted as a cross-linking agent, inducing structural rearrangements and enhancing the development of mesopores. This process enhanced the specific surface area as well as introduced different functional groups, such as $-\text{OH}$, $-\text{COOH}$, and phosphate groups, that serve as functional sites for pollutant binding. The resulting AC was then rinsed with 0.1% sodium bicarbonate to eliminate unreacted chemicals, rinsed with distilled water, dried, and pulverized.

The magnetic activated carbon was prepared by adding 50 ml of water, 1.39 g of ferrous sulfate heptahydrate, and 2.78 g of activated carbon into a 250 ml beaker, subsequently stirring for 15 min using a magnetic stirrer. Next, 10 mL of 2 M sodium hydroxide was poured in, and the contents were incubated at 353 K for 1 h. Under these alkaline conditions, the ferrous ions underwent hydrolysis and oxidation, promoting the in situ synthesis of iron oxides. Simultaneously, the iron oxides interacted with the oxygenated surface functional groups ($-\text{OH}$, $-\text{COOH}$, $-\text{PO}_4^{3-}$) of the activated carbon, facilitating complex formation and anchoring of the magnetic particles onto the carbon matrix. This process imparted magnetic properties to the activated carbon while preserving its high surface area and porosity. After incubation, the material was washed with distilled water to remove excess alkali, then dried and stored in an airtight container. The resulting magnetic activated carbon was designated as *Af*-MAC, and the overall synthesis steps are shown in Fig. 1.



Fig. 1 Synthesis of magnetic AC from *Acacia falcata* biomass

2.3 Characterization

The surface morphology of the adsorbent was investigated using a Neon 40 field emission scanning electron microscope (FE-SEM) by Carl Zeiss (Germany), while the elemental composition was determined through energy-dispersive X-ray spectroscopy (EDS) using an instrument from Oxford Instruments (UK). Textural properties, including specific surface area, pore volume, and pore size distribution, were evaluated using the Brunauer–Emmett–Teller (BET) method, with measurements carried out on a surface area analyzer provided by Smart Instruments (India). Fourier transform infrared spectroscopy, with an instrument from Agilent Technologies, USA, was employed for surface group analysis of Af–MAC. The magnetic properties were recorded with the aid of a Vibrating Sample Magnetometer (VSM 8600, Lakeshore Cryotonic, USA). X-ray photoelectron spectroscopy (XPS) analysis was performed using a K- α 149 spectrometer (Thermo Fisher Scientific, UK) to investigate the surface chemical composition and the electronic states of the constituent elements in the material. The atomic and molecular structure was analyzed using XRD spectra (D8 Advance, Bruker, Germany). Cr(VI) concentration was assessed by employing a UV-visible spectrophotometer from Eppendorf (Xenon flash lamp, CMOS photodiode array). The pH-zero-point charge (pH_{ZPC}) of Af–MAC was evaluated using the drift method (Samanth et al., 2023).

2.4 Cr(VI) batch adsorption studies

Cr(VI) removal studies utilizing Af–MAC were carried out in 100 mL solutions at 303 K and 150 rpm agitation in 250 mL conical flasks unless stated otherwise.

pH studies The pH of 100 mL Cr(VI) solution (10 mg/L) was tuned to range from 2 to 12 using HCl and NaOH. Subsequently, 0.3 g/L of Af–MAC was added to adsorb Cr(VI) for 3 h.

Influence of adsorbent dose Cr(VI) solutions were modified to the optimal pH. Different doses (0.1, 0.2, 0.3, 0.4, and 0.5 g/L) of Af–MAC were then introduced into a 100 ml solution, followed by a 3 h adsorption period.

Effect of contact time and initial Cr(VI) concentrations Experiments were conducted at the optimum dose of Af–MAC and pH by varying contact duration time (5 to 180 min) and Cr(VI) concentrations (5 to 25 mg/l).

Effect of temperature The influence of temperature of Cr(VI) solution was studied over a range of 293–323 K, under optimal dosage and pH conditions, for 3 h.

2.5 Adsorption models

Adsorption models like kinetic, isotherm, and thermodynamic models are essential in understanding the competence of Af–MAC to adsorb Cr(VI) from wastewater. Together, these models enable comprehensive insights into adsorption mechanisms, efficiency, and limitations, which are crucial for the development of sustainable adsorption systems for water treatment.

2.5.1 Kinetic models

Kinetic model equations, like Pseudo First Order (PFO), Pseudo Second Order (PSO), and Intra-particle Diffusion (IPD) models, are essential for analyzing adsorption processes. Summarized in Table 1, these models help determine adsorption rates and underlying mechanisms, distinguishing physical from chemical interactions (Jun et al., 2024). The PFO model suggests adsorption based on available sites, while the PSO model indicates chemisorption. The IPD model further identifies diffusion limitations within adsorbent pores.

2.5.2 Advanced statistical physics isotherm models

Classical isotherms, which comprise Langmuir and Freundlich models, are extensively employed to explain adsorption based on simplified assumptions like monolayer adsorption, uniform adsorption sites, or surface heterogeneity. These models provide a good fit for experimental data in straightforward systems but are limited in their ability to account for complex interactions between adsorbate molecules or surface irregularities (Dhaouadi et al., 2024). On the other hand, advanced statistical physics isotherms, such as one-layer one energy (OLOE), two-layer one energy (TLOE), and two-layer two energy (TLTE) models, offer a more detailed understanding of adsorption by considering multilayer adsorption, surface heterogeneity, and adsorbate-adsorbate interactions (Yanan et al., 2023), (Sellaoui et al., 2021). The model equations are presented in Table 1.

In the OLOE model, interactions occur only among the adsorbent surface and Cr(VI) molecules, forming a single layer. In contrast, the TLOE and TLSE models allow for the formation of a second layer due to Cr(VI) molecule interactions. Advanced statistical physics model parameters enable the study of orientation, site density, and adsorption energies of binding sites. The parameter n , representing the count of binding sites, is important for understanding the orientation of Cr(VI) binding to adsorption sites (Selvaraj et al., 2024).

Table 1 Kinetic, thermodynamic, and advanced statistical physics isotherm models

Kinetic Models	
Model	Model Equation
Pseudo First Order	$q_t = q_e \left(1 - e^{-k_1 t} \right)$
Pseudo Second Order	$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1}$
Intra-particle diffusion	$q_t = k t^{0.5} + c$
Advanced statistical physics isotherm model	
Model	Model Equation
One layer with one energy (OLOE) model	$q_e = \frac{n D_s}{1 + \left(\frac{C_{1/2}}{C_e} \right)^n}$
Two layer with one energy (TLOE) model	$q_e = n D_s \frac{\left(\frac{C_e}{C_{1/2}} \right)^n + 2 \left(\frac{C_e}{C_{1/2}} \right)^n}{1 + \left(\frac{C_e}{C_{1/2}} \right)^n + \left(\frac{C_e}{C_{1/2}} \right)^n}$
Two layers with two energy (TLTE) model	$q_e = n D_s \frac{\left(\frac{C_e}{C_{1/2}1} \right)^n + \left(\frac{C_e}{C_{1/2}2} \right)^n}{1 + \left(\frac{C_e}{C_{1/2}1} \right)^n + \left(\frac{C_e}{C_{1/2}2} \right)^n}$
Thermodynamic model	
Model	Model Equation
Van't Hoff equation	$K_T = \exp \left[\left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R T} \right) \right]$
q_t (mg/g): adsorption capacity as a function of time; q_e (mg/g): adsorption capacity at equilibrium; t (min); k_1 (l/min); PSO rate constant; k_2 (g/mg min ^{0.5}); PFO rate constant; k_1 (g/mg min): IPD rate constant; c (mg/g): IPD intercept; q_e (mg/g): adsorption capacity at equilibrium; n : number of adsorbate molecules attached to adsorption site; D_s (mg/g): receptor site density at saturation; C_e (mg/L): equilibrium concentration; $C_{1/2}$: half-saturation concentration for TLOE model; $(C_{1/2})_1$ and $(C_{1/2})_2$: half-saturation concentration for TLTE model; ΔG° (kJ/mol): ($= - RT \ln K_T$), standard Gibbs free energy; K_T : (q_e/C_e), distribution factor; ΔH° (kJ/mol): standard enthalpy; ΔS° (J/mol): standard entropy; R (J/mol): Ideal gas constant; T (K): Temperature	

When n is less than 1, Cr(VI) molecules are anchored at the binding sites at an inclined orientation, whereas for $n > 1$, the molecules attach in a horizontal orientation (Knani et al., 2024). Here, D_s represents the site density (number density of each binding site), and ΔE denotes the binding energy of each site. Understanding these parameters is essential for examining interactions at the microscopic level (Seliem & Mobarak, 2019). Although these models are mathematically complex, they provide valuable insights into adsorption mechanisms, energy distributions, and surface properties, making them highly effective for analyzing intricate adsorption processes.

2.5.3 Thermodynamic model

Thermodynamic models, with equations and parameters shown in Table 1, are essential for assessing Cr(VI) adsorption feasibility and nature. Parameters like standard Gibbs free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°) reveal spontaneity and endothermic or exothermic nature. Negative ΔG° confirms spontaneity, while positive

ΔH° suggests improved efficiency at higher temperatures. Positive ΔS° indicates increased randomness (Selvaraj et al., 2023).

2.6 Regeneration studies

The regeneration of Af–MAC, essential for environmental and industrial applications, reduces costs and waste by enabling adsorbent reuse. The adsorption process was examined in 250 mL flasks under controlled conditions for 3 h. Desorption of the adsorbed Cr(VI) from Af–MAC was achieved through treatment with 0.1 M NaOH (100 mL) for a duration of 1 h. Following desorption, Af–MAC was rinsed with distilled water, oven-dried, and subsequently used for the consequent batch experiment.

2.7 Effect of ions

Batch studies were conducted to investigate Cr(VI) removal efficiency in the presence of various cations and anions, including Na^+ , K^+ , Ca^{2+} , SO_4^{2-} , NO_3^- , CO_3^{2-} , and PO_4^{3-} , which are common in industrial effluents. The studies involved mixing 0.5 g/L Af–MAC with 100 mL Cr(VI) solutions (10 ppm) containing 50 ppm of co-existing ions, at pH 2, under optimum conditions. Post-experiment, Cr(VI) removal percentage, and Af–MAC's adsorption capacity were calculated.

2.8 Cr(VI) removal from different water bodies

Water samples from Arabi Falls, Manipal Lake, Swarna River, and well water were used to prepare 10 ppm Cr(VI) solutions for studying Cr(VI) removal with Af–MAC. Each solution, adjusted to pH 2, contained 0.5 g/L of Af–MAC and was studied at optimum conditions. The effectiveness of Cr(VI) adsorption and Af–MAC's adsorption performance were examined pertaining to each diverse source in comparison to distilled water.

3 Results and discussions

3.1 Af–MAC surface analysis

XRD patterns (Fig. 2a) of Af–MAC before and after Cr(VI) uptake show substantial alterations in amorphous carbon structure. Initially, broad peaks corresponding to the (002) and (100) planes are observed at 25.49° and 42.73° , with d-spacings of 3.49 Å and 2.12 Å, respectively.

Similar peaks were observed for phosphoric acid-treated jute fibers (Chen et al., 2020) and coffee grounds (Zięzio et al., 2020). After Cr(VI) adsorption, the (002) peak shifted to 25.41° , indicating a slight increase in d-spacing to 3.51 Å, which suggests a minor expansion of the interlayer distance in the graphene structure. In contrast, the (100) crystal plane shifts to 43.28° , with a decrease in d-spacing to 2.09 Å. These observations reflect subtle modifications in the carbon peak due to Cr(VI) uptake, with changes in interlayer spacing. Furthermore, the peak intensity corresponding to (002) and (100) crystal planes changed; This might result from the interaction of functional groups of carbon with chromium moi-

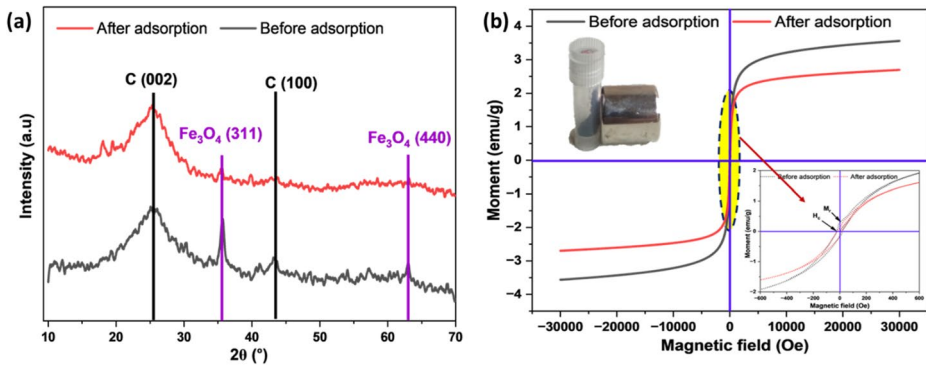


Fig. 2 XRD (a) and VSM (b) analysis of Af–MAC for Cr(VI) removal

eties. In addition, peaks corresponding to Fe_3O_4 nanoparticles are observed in the XRD spectrum. Before Cr(VI) adsorption, distinct diffraction peaks at 35.63° and 62.91° for the (311) and (440) planes, respectively, indicate lattice parameters of $8.37 \text{ \AA}$, a crystallite size of 17.9 nm , and a cell volume of $585.96 \text{ \AA}^3$. After Cr(VI) adsorption, shifts in these peaks to 35.43° and 62.23° , along with a reduction in crystallite size to 8.21 nm and an increase in lattice parameter to $8.421 \text{ \AA}$. The cell volume expanded to $597.16 \text{ \AA}^3$, suggesting lattice distortion and potential incorporation of Cr species into the Fe_3O_4 structure, leading to increased lattice strain and expansion (Samanth et al., 2024).

VSM analysis was used to evaluate the magnetic properties of Af–MAC, as illustrated in Fig. 2b. Initially, Af–MAC exhibited a coercivity (H_c) of 20.28 Oe , remanence (M_r) of 0.31 emu/g , and saturation magnetization (M_s) of 3.53 emu/g . Af–MAC exhibited a higher saturation magnetization compared to magnetic activated carbon (3.01 emu/g) made from commercial activated carbon (Saucier et al., 2017). The nonexistence of a distinct hysteresis loop indicates superparamagnetic behavior (Wang et al., 2021a, b), as shown in the bottom-right inset of Fig. 2b. The VSM results confirm the presence of Fe_3O_4 nanoparticles on Af–MAC, consistent with the peaks corresponding to Fe_3O_4 in the XRD spectrum. This magnetic property makes Af–MAC particularly advantageous for magnetic separation, as it can be easily magnetized and demagnetized. After Cr(VI) adsorption, the magnetic properties further declined: H_c decreased to 15.72 Oe , M_r to 0.12 emu/g , and M_s to 2.67 emu/g . The hysteresis-free magnetization curve after post-adsorption confirms the retention of superparamagnetic behavior, albeit with reduced magnetic strength. The decrease in coercivity and saturation magnetization is likely due to the surface coverage by non-magnetic chromium complexes, which interfere with the magnetic domains.

The surface morphology of pristine Af–MAC is examined using FESEM, revealing the presence of microcracks and pits as shown in Fig. 3a, likely caused by phosphoric acid and thermal treatments of the biomass. These processes induce pore formation by breaking down chemical components and evaporating volatile substances, resulting in a porous network that enhances adsorption (Ibrahim et al., 2023). The formation of spherical nanoparticles (Fig. 3a inset), which were dispersed and aggregated on the Af–MAC surface, was attributed to the precipitation of Fe_3O_4 nanoparticles during the modification of the adsorbent. The average size of Fe_3O_4 nanoparticles embedded in Af–MAC was 51.14 nm . These nanoparticles enhance the adsorption properties of Af–MAC by increasing surface area and

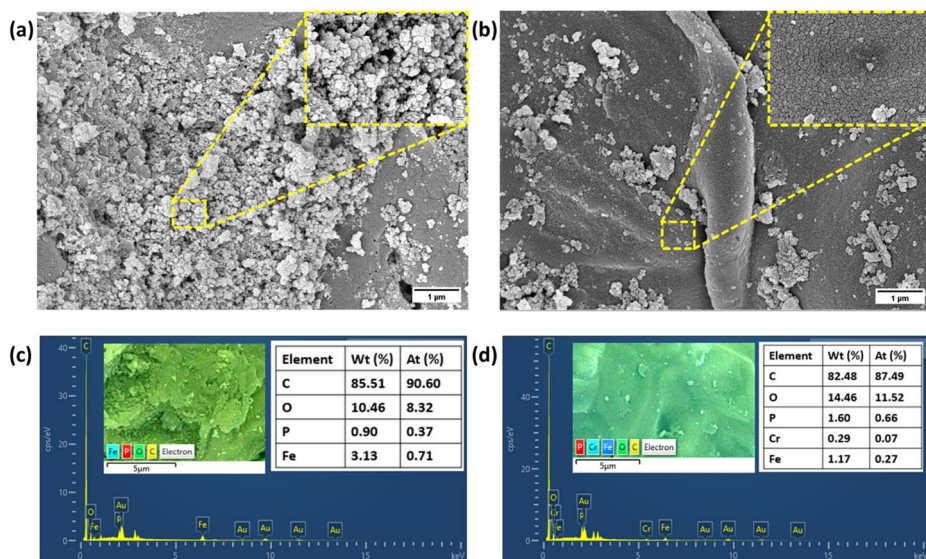


Fig. 3 FESEM analysis of bare Af–MAC (a), after Cr(VI) adsorption (b), EDS analysis of bare Af–MAC (c), after Cr(VI) adsorption (d)

active sites (Tran et al., 2018). After Cr(VI) adsorption, significant changes were observed (Fig. 3b), including a smoother surface with reduced micro-cracks and pores. The observed change is attributed to the incorporation and the uptake of Cr(VI) ions to surface functional groups, prompting the generation of surface-chromium species and precipitation of chromium oxides, ultimately yielding a more compact structure (Nasseh et al., 2021), (Isaac & Siddiqui, 2022).

The EDS spectrum of Af–MAC before Cr(VI) removal (Fig. 3c), reveals a high carbon content (85.51% by weight) with significant oxygen (10.46% by weight) and smaller amounts of phosphorus (0.90% by weight) and iron (3.13% by weight), attributed to phosphoric acid modification and Fe_3O_4 nanoparticle formation (Selvaraj et al., 2023). Following Cr(VI) adsorption (Fig. 3d), the carbon content slightly decreases to 82.48% by weight, while oxygen increases to 14.46% by weight, indicating the formation of chromium-oxygen complexes and precipitation of chromium oxides. Additionally, the EDS results exhibit two separate peaks related to chromium at 0.57 keV and 5.41 keV. The appearance of these peaks confirms the successful adsorption of chromium (0.29% by weight). The observed changes in elemental composition, coupled with chromium peak emergence, confirm successful Cr(VI) adsorption onto Af–MAC.

Af–MAC demonstrates a large specific surface area (SSA) of 472.98 m^2/g , which enhances its adsorption capacity by providing large binding sites for interaction with Cr(VI) ions. Notably, Af–MAC exhibits a higher SSA compared to other magnetic-activated carbon derived from orange peels (155.09 m^2/g) (Khalil et al., 2023), pine fruit waste (182.5 m^2/g) (Hashemzadeh et al., 2024), and Sapelli wood sawdust (331.5 m^2/g) (Nascimento et al., 2023). The high pore volume (0.3557 cm^3/g) indicates the Af–MAC's capability to accommodate a significant amount of adsorbate within its structure. Af–MAC's mesoporous structure, characterized by a 3.01 nm pore diameter, is ideal for accommodating

larger species like Cr(VI) ions. Post Cr(VI) adsorption, SSA and pore volume reduced to 419.52 mg/g and pore volume 0.004 cm³/g, respectively. The observed reduction in SSA and pore volume is attributed to the occupation of pores by chromium ions, which is consistent with the FESEM surface micrograph obtained post-Cr(VI) uptake.

Figure 4a depicts the FTIR spectra of Af–MAC pre- and post-Cr(VI) uptake. The spectrum reveals several functional groups: hydroxyl (-OH) and amine (-NH) groups between 3600 and 3400 cm⁻¹, nitrile (-C≡N) and isocyanate (-N=C=O) groups between 2409 and 2287 cm⁻¹, and C=C, C=O, and C=N groups from 1681 to 1560 cm⁻¹ (Liu et al., 2024), (Patra et al., 2020). Additionally, C-O, C-H, and P-O-C groups appear between 1470 and 1320 cm⁻¹ (Liu et al., 2024). Post-Cr(VI) adsorption, the spectrum exhibits diminished peak intensities and subtle peak shifts, attributed to surface functional group-mediated Cr(VI) reduction and subsequent chromium complexation.

Af–MAC was subjected to XPS analysis pre- and post-Cr(VI) adsorption, with detailed results displayed in the high-resolution survey spectrum (Fig. 4b). Before adsorption, the surface of Af–MAC showed binding energies of 285.1 eV for carbon, 531.14 eV for oxygen, 724.88 (Fe 2p_{1/2}) and 711.48 eV (Fe 2p_{3/2}) for iron, 133.92 eV for phosphorus, and 399.51 eV for nitrogen (Elhamdy, 2024), (Ozpinar et al., 2022), with atomic percentages of 66.34%, 23.28%, 6.67%, 1.88%, and 1.83%, respectively. Following Cr(VI) uptake, the emergence of two distinct chromium peaks at 588.98 eV (Cr 2p_{1/2}) and 578.2 eV (Cr 2p_{3/2}), comprising 0.62% atomic concentration, demonstrates successful Cr(VI) adsorption (Li et al., 2021). Shifts in binding energies for oxygen from 531.14 to 531.85 eV and for iron from 711.48 to 711.86 eV suggest that functional groups of these elements participated in Cr(VI) to Cr(III) reduction.

Figure 4c displays the deconvoluted XPS spectrum of Cr(VI)-loaded Af–MAC. The analysis reveals important details about the surface chemistry of Af–MAC. For P 2p, the bonds are identified as P=O at 134.42 eV (39.74%) and P-O at 133.54 eV (60.26%), indicat-

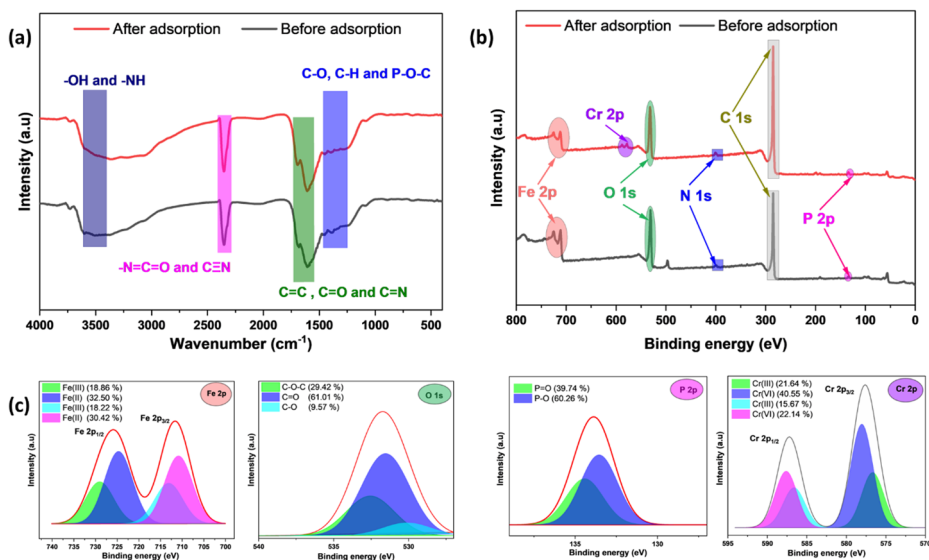


Fig. 4 FTIR analysis (a), XPS survey spectra of Af–MAC (b) and deconvolution of Fe 2p, Cr 2p, O 1s and P 2p after Cr(VI) uptake (c)

ing a significant presence of P-O groups involved in the Cr(VI) removal (Zuo et al., 2023). The O 1s analysis reveals three bonding environments: C-O-C at 532.55 eV (29.42%), C=O at 531.53 eV (61.00%), and C-O at 530.10 eV (9.57%), highlighting the predominance of oxygenated functional groups that interact with Cr(VI) (Zhang et al., 2024). Cr 2p peaks belonging to Cr(VI) are detected at 587.62 eV (22.14%) and 578.03 eV (40.55%), while Cr(III) is detected at 586.61 eV (15.67%) and 576.66 eV (21.64%), indicating a partial reduction of Cr(VI) (Elhamdy, 2024). Fe 2p shows both Fe(III) at 729.02 eV (18.86%) and 713.10 eV (18.22%) and Fe(II) at 724.67 eV (32.50%) and 710.84 eV (30.42%), reflecting active redox processes.

3.2 Adsorption analyses

3.2.1 Effect of operational conditions

The pH of the solution significantly governs Cr(VI) removal, influencing both chromium speciation and adsorbent surface charge, which significantly impacts the adsorbent's capacity for Cr(VI) removal. At below 2 pH, HCrO_4^- predominates, and the Af-MAC surface has a net positive charge, enhancing electrostatic attraction and adsorption efficiency. Between pH 3 and 7, a dynamic equilibrium between HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ exists, with a potentially less positive adsorbent surface, reducing adsorption. Above pH 7, the solution is predominantly composed of CrO_4^{2-} ions, causing the Af-MAC surface to become negatively charged and inducing repulsive electrostatic forces that hinder Cr(VI) adsorption (Mancilla et al., 2022).

pH-dependent Cr(VI) removal was studied using Af-MAC as an adsorbent, over a pH range from acidic to alkaline (2–12). As shown in Fig. 5a, the results revealed a distinct pH-dependent trend in both Cr(VI) removal performance and adsorption capacity. Af-MAC showed exceptional performance at pH 2, achieving a remarkable Cr(VI) removal of 85.45% and a high adsorption capacity (28.48 mg/g). The exceptional removal potential at acidic pH is attributed to the surface protonation of Af-MAC's functional moieties, conferring a positive surface charge and strengthening electrostatic interactions with anionic Cr(VI), notably with HCrO_4^- ions (Li et al., 2019). Upon pH rise, surface protonation decreased, diminishing the positive surface potential and reducing electrostatic forces, causing a pronounced drop in adsorption performance to 20.31% (6.68 mg/g) at pH 12. Furthermore, at higher pH levels, hydroxyl ions compete for binding sites on Af-MAC, further hindering the adsorption process (Li et al., 2019). The maximum removal observed at pH 2 aligns with outcomes reported in recent literature (Sangkarak et al., 2024), (Wang et al., 2021a, b).

Figure 5b illustrates the zero-point charge (pH_{ZPC}) of Af-MAC, which was estimated as 6.96. At pH values below this point, Af-MAC is positively charged, whereas it acquires a negative charge above this threshold (Rzig et al., 2024). Below pH_{ZPC} , protonation of Af-MAC's surface functional groups (-OH, $-\text{NH}_2$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{C}-\text{O}-\text{C}$) generates a positive surface charge, increasing electrostatic affinity for anionic Cr(VI) species (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) and enhancing adsorption and reduction efficiency (Wang et al., 2021a, b). Conversely, at pH above 6.96, Af-MAC's surface is negatively charged, which reduces its interaction with Cr(VI) and leads to decreased adsorption. Additionally, higher pH levels may cause competition from hydroxyl ions and precipitation of Cr(III), further diminishing effectiveness (Sangkarak et al., 2024).

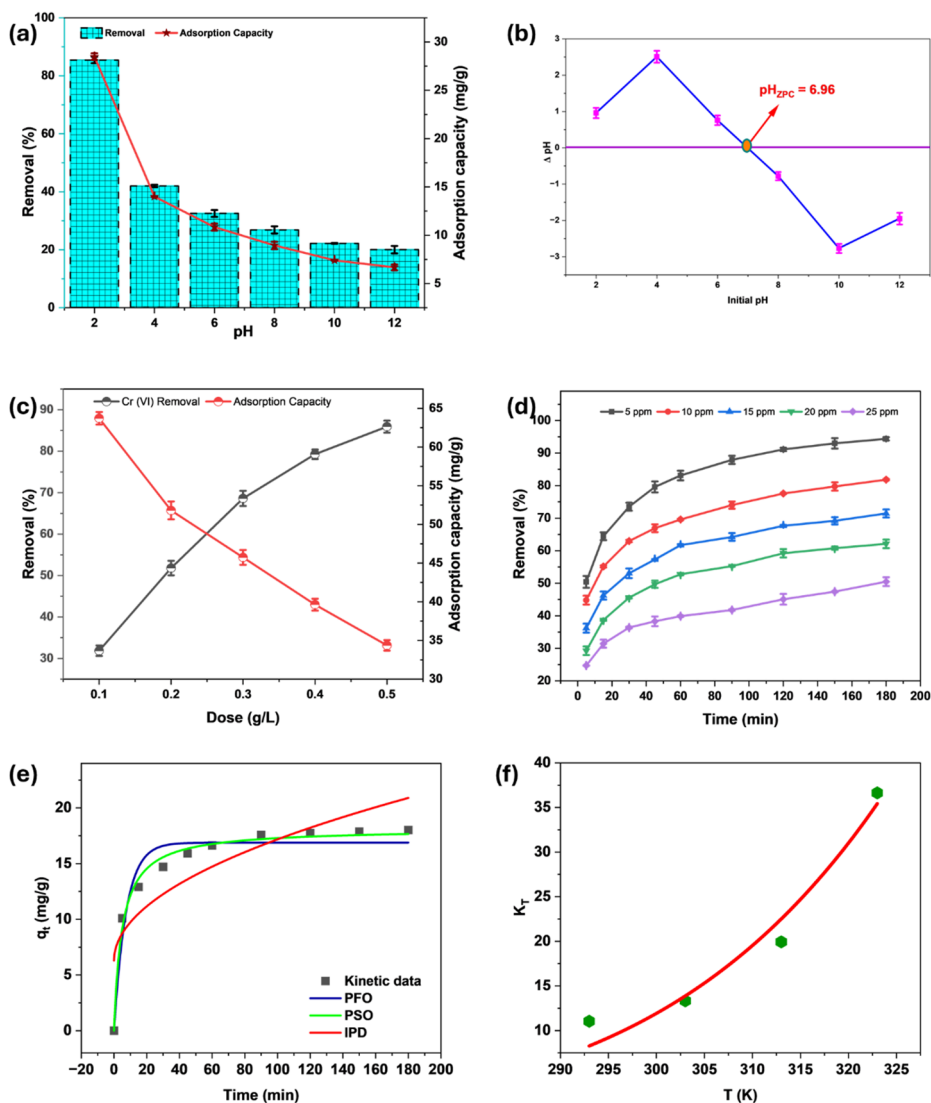


Fig. 5 Cr(VI) adsorption using Af-MAC: Effect of initial pH (a), zero-point charge (b), effect of Af-MAC dose (c), effect of initial Cr(VI) concentration and time (d), kinetic models (e), and thermodynamic model (f)

Figure 5c shows the effect of Af-MAC dosage (0.1–0.5 g/L), illustrating the optimal dosage for maximum removal efficiency. The data reveal a substantial increase in Cr(VI) adsorption, climbing from 31.86 to 85.93% as Af-MAC dose rises, which is due to the rise in density of binding sites, leading to stronger interactions and more efficient sequestration of Cr(VI) species (Vinayagam et al., 2022). However, the adsorption capacity decreases from 63.72 to 34.37 mg/g with increasing dosage. This reduction is because, at higher doses, a larger proportion of binding sites remain unoccupied, leading to less efficient utilization of the adsorption sites (Vinayagam, Murugesan, Vinayagam et al., 2022a, b). Conversely, at

lower doses, the binding sites are more fully utilized, resulting in higher adsorption capacity but lower removal efficiency owing to the reduced number of active binding sites. Af–MAC dosage of 0.25 g/L was selected to optimize chromium removal performance and adsorbent capacity for subsequent investigations.

A series of Cr(VI) removal studies was undertaken within a concentration range of 5–25 mg/L to assess the impact on removal percentage and adsorption capacity. As shown in Fig. 5d, the results show a clear trend, where Cr(VI) uptake potential declines upon increasing the concentration. Specifically, at the minimum concentration, 5 mg/L, the removal is high at 90.07%. However, as the concentration rises to 25 mg/L, the Cr(VI) adsorption drops to 50.50%. The reduction in efficiency at higher concentrations arises from the complete occupation of available binding sites on Af–MAC (Thottathil et al., 2024), (Suganya et al., 2020). Furthermore, the adsorption capacity rises from 18.01 mg/g at 5 mg/L to 50.51 mg/g at 25 mg/L. This enhancement is because of the higher concentration of Cr(VI) molecules, which provides a greater concentration gradient for mass transfer and enables more ions to bind to the Af–MAC active sites.

The trend shown in Fig. 5d indicates that although the initial adsorption rate is rapid, it slows down as the binding sites become occupied. Notably, the majority of adsorption occurred within the initial 30 min, with this swift removal credited to the large number of binding spots. With increasing contact time, the adsorption rate reaches equilibrium, indicating that the active sites are becoming saturated (Khalil et al., 2022). After 180 min, equilibrium is reached, with no substantial rise in Cr(VI) removal was recorded.

3.2.2 Investigation of kinetic and thermodynamic models

To assess the Cr(VI) adsorption kinetics on Af–MAC, a detailed analysis was performed employing three kinetic model equations: PFO, PSO, and IPD, and the key findings from the kinetic modeling are presented in Table 2; Fig. 5e. The PFO model yielded a q_e value of 16.88 mg/g, an R^2 of 0.949, and a χ^2 of 1.794. Although this model fits the experimental data reasonably well, the R^2 value suggests that it may not fully capture the adsorption kinetics. In contrast, the PSO model showed an apt fitting, with an R^2 of 0.989 and a remarkably lower χ^2 value of 0.368. Notably, the experimental q_e (18.01 mg/g) showed excellent agreement with the model q_e (18.14 mg/g) from the PSO kinetic equation, demonstrating its strong predictive capability. PSO model reveals that, the binding of Cr(VI) on the Af–MAC through electrostatic interactions by sharing electrons between surface functional moieties and Cr(VI) ions (Tian et al., 2024), (Afshin et al., 2021). The IPD model demonstrated the weakest correlation with the experimental data, yielding an R^2 of 0.627 and a χ^2 of 2.142. This suggests that intra-particle diffusion plays a minor part in the Cr(VI) removal.

Thermodynamic investigations of Cr(VI) adsorption by Af–MAC were performed between 293 and 323 K. The negative ΔG° (−5.85 to −9.67 kJ/mol) presented in Table 2 confirms the spontaneity. The increase in ΔG° negativity with temperature indicates an enhanced adsorption process at elevated temperatures (Ramya et al., 2022). The positive ΔH° (3.813 kJ/mol) implies an endothermic process. The positive ΔS° (147.73 J/mol K) reveals an enhancement in disorder at the Af–MAC–water interface during Cr(VI) adsorption, indicating a favorable entropic contribution (Vinayagam et al., 2023). Figure 5f illustrates that the thermodynamic equilibrium constant (K_T) increases as the temperature increases, further confirming the endothermic adsorption of chromium moieties.

Table 2 Kinetic and thermodynamic model parameters of Cr(VI) removal

Kinetic models					
		Parameters			
PFO	k_1 (min^{-1})	0.135			
	Model: q_e (mg/g)	16.88			
	Exp: q_e (mg/g)	18.01			
	R^2	0.949			
	χ^2	1.794			
	RMSE	1.198			
PSO	k_2 (g/mg.min)	0.011			
	Model: q_e (mg/g)	18.14			
	Exp: q_e (mg/g)	18.01			
	R^2	0.989			
	χ^2	0.368			
	RMSE	0.544			
IPD	k ((mg/g) $\text{min}^{0.5}$)	0.598			
	c (mg/g)	10.98			
	R^2	0.627			
	χ^2	2.142			
	RMSE	3.603			
Thermodynamic model					
T (K)		293	303	313	323
ΔG° (kJ/mol)		- 5.85	- 6.52	- 7.79	-9.67
ΔH° (kJ/mol)		3.813			
ΔS° (J/mol K)		147.73			

3.2.3 Advanced statistical physics isotherm models

The adsorption isotherm dataset for Cr(VI) was fitted with advanced statistical models, namely OLOE, TLOE, and TLTE, with the corresponding results depicted in Fig. 6a. Table 3 summarizes the corresponding R^2 and χ^2 of advanced statistical isotherm models at various temperatures. Notably, the TLOE model demonstrated superior fit, yielding higher R^2 (0.997 to 0.999) and lower χ^2 (0.003 to 1.262) values, surpassing the other two models across all temperatures. These findings indicate that Cr(VI) ions bind to the Af-MAC in a two-layer configuration. The parameters of TLOE models (n , D , Q_{sat}) and binding energy (ΔE) explain the characteristics of the Cr(VI) removal mechanism, and the parameters are presented in Table 4.

The value of n is crucial in determining the adsorption geometry and binding mechanisms of Cr(VI) ions onto Af-MAC, influencing the spatial arrangement and interaction. When $n < 0.5$, the ions adopt a parallel orientation, engaging in a multi-docking mechanism. In contrast, n values greater than 1 correspond to a non-parallel orientation, characterized by multi-molecular interactions (Seliem & Mobarak, 2019). Interestingly, an intermediate binding mode is observed when $0.5 \leq n \leq 1$, where the adsorbate exhibits both parallel and non-parallel orientation, indicating a transitional binding behavior (Piazzzi Fuhr et al., 2024), (Yazidi et al., 2020). Figure 6b illustrates a notable trend in the temperature-dependent variation of the parameter n . When the temperature is elevated from 293 to 323 K, the n value decreases steadily from 0.385 to 0.231. This consistent decline indicates enhanced adsorption affinity and alters surface interactions. Notably, since n remains below 0.5 across the

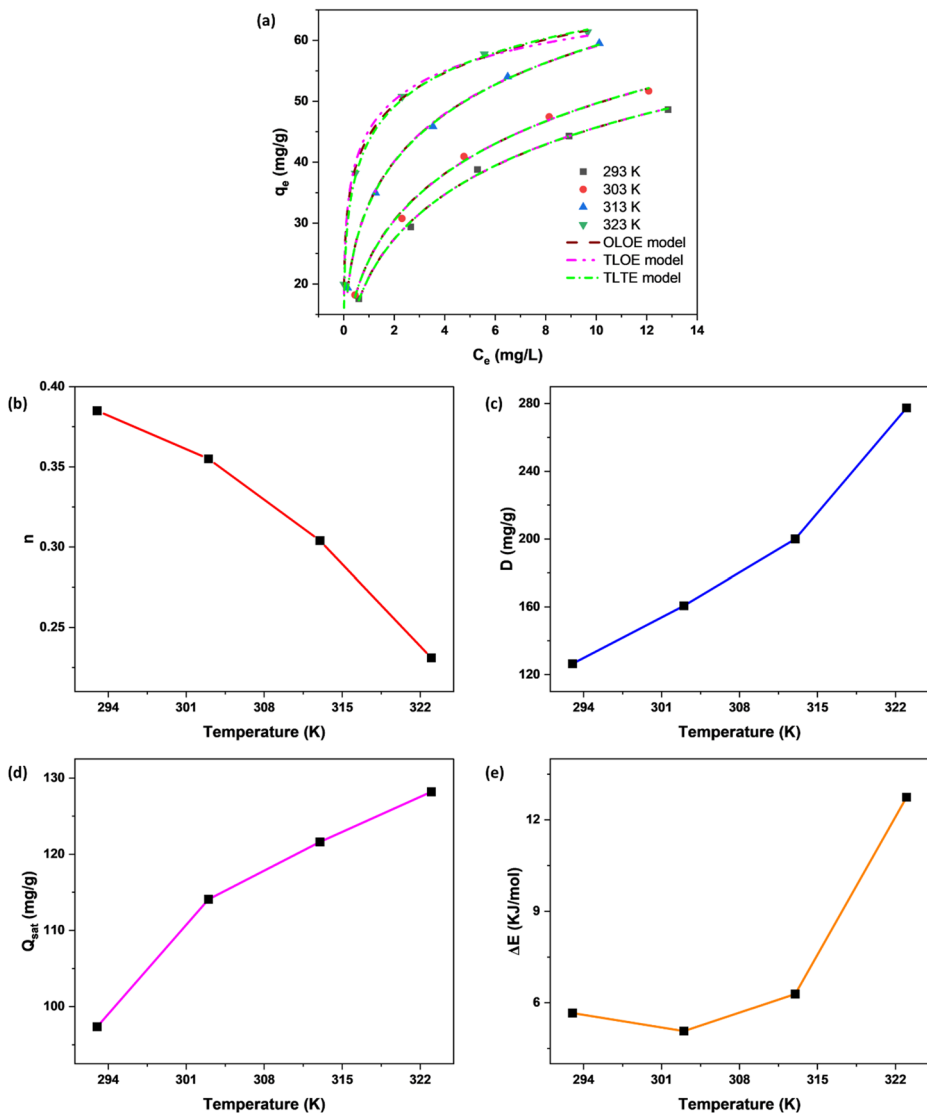


Fig. 6 Influence of temperature on Cr(VI) uptake: Isotherm (OLOE, TLOE, and TLTE) models (a); steric parameter, n (b), receptor site density, D (c), adsorption saturation capacity, Q_{sat} (d) and adsorption binding energy, ΔE (e)

temperature range, Cr(VI) species bind to the surface in a parallel orientation, characterized by a multi-docking mechanism.

The steric parameter D , denoting the Cr(VI) ion density per active binding site on Af-MAC, displays an inverse correlation with n , indicating that increasing n values reduce Cr(VI) moieties bound to each site (Jethave et al., 2023). Notably, Fig. 6c reveals a significant temperature-dependent trend, where D rises substantially from 126.45 mg/g at 293 K to 277.47 mg/g at 323 K. This substantial increase in D is attributed to enhanced kinetic energy

Table 3 Regression coefficient and chi-square values for Cr(VI) adsorption using advanced statistical physics isotherm models

Temperature (K)	293			303			313			323		
	R ²	χ^2	RMSE	R ²	χ^2	RMSE	R ²	χ^2	RMSE	R ²	χ^2	RMSE
OLOE model	0.997	0.834	0.336	0.996	1.363	0.438	0.998	0.527	0.334	0.994	3.021	1.341
TLOE model	0.998	0.777	0.334	0.997	1.262	0.336	0.999	0.003	0.201	0.998	0.656	0.334
TLTE model	0.997	1.553	0.536	0.996	2.519	1.338	0.996	0.828	0.338	0.986	15.79	1.836

of Cr(VI) moieties in solution and reduced mass transfer resistance, facilitating Cr(VI) moieties transport from the bulk solution to Af–MAC surface. Consequently, receptor site density doubles, indicating that Cr(VI) moieties attached to each binding site nearly double with increasing temperature.

Figure 6d demonstrates that the Q_{sat} of Af–MAC increases significantly with temperature, indicating enhanced adsorption efficiency. The positive relationship between temperature and adsorption capacity confirms endothermic adsorption and the same was observed in thermodynamic studies. The Q_{sat} value rises from 97.37 mg/g at 293 K to 128.19 mg/g at 323 K. This adsorption capacity is substantially higher than those reported for many other adsorbent materials, as summarized and compared in Table 5.

Figure 6e illustrates the temperature-dependent variation of adsorption energy (ΔE) at the interface of Cr(VI) ions and Af–MAC surface sites, calculated using half-saturation concentration. A notable increasing trend is observed, with ΔE rising from 5.66 kJ/mol at 293 K to 12.74 kJ/mol at 323 K. This enhancement indicates an improved affinity for Cr(VI) moieties to bind with adsorption sites at elevated temperatures. Furthermore, the adsorption energy values (<20 kJ/mol) indicate that hydrogen bonding and electrostatic interactions are the dominant forces driving Cr(VI) adsorption onto Af–MAC (Georgin et al., 2021).

3.2.4 Possible adsorption mechanism

The Cr(VI) removal mechanism by Af–MAC involves several processes that work together to facilitate effective adsorption, as shown in Fig. 7. These processes include electrostatic attraction, pore filling, conversion of Cr(VI) to Cr(III), chromium oxides precipitation, chromium complexes, and hydrogen bonding. In acidic conditions, the Af–MAC surface features protonated functional moieties, like hydroxyl, carbonyl groups, amine groups (-NH_2), and Fe_3O_4 nanoparticles, which attract Cr(VI) moieties (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) through electrostatic interactions. Once adsorbed, the Cr(VI) moieties transform Cr(III), aided by the protonation of functional moieties on Af–MAC (Nasseh et al., 2021). The reduced Cr(III) species precipitate as oxides of chromium (Cr_2O_3 and Cr(OH)_3) and some form stable complexes with surface functional groups. Additionally, chromium species and oxides of chromium interact via hydrogen bonding with surface functional groups (Isaac & Siddiqui, 2022).

The chromium removal mechanism is supported by various characterization techniques. The FESEM micrograph after Cr(VI) uptake revealed a smoother surface and a reduction in micropores and cracks, owing to the filling of pores with Cr(VI) ions, precipitation of chromium oxides, and chromium binding with surface functional moieties. Additionally, EDS and XPS spectra substantiate the binding and reduction of Cr(VI). Deconvolution of the chromium peak further reinforces Cr(VI) reduction and adsorption (Elhamdy, 2024). XRD data showed the formation of Fe_3O_4 nanoparticles, and the intensity of peaks was reduced after Cr(VI) uptake, corroborating the Cr(VI) removal and generation of chromium complexes. FTIR peak shifts and changes in intensities further supported the participation of functional moieties in the adsorption and reduction of Cr(VI) (Liu et al., 2024). These combined mechanisms and characterizations explain the high Cr(VI) removal by Af–MAC.

Table 4 Two layer one energy isotherm model parameters for Cr(VI) removal at various temperatures

Temperature (K)	293	303	313	323
n	0.385	0.355	0.304	0.231
D (mg/g)	126.45	160.69	200.01	277.47
$Q_{\text{sat}} = 2 n D$ (mg/g)	97.37	114.09	121.61	128.19
$C_{1/2}$ (mg/L)	12.71	17.36	11.60	1.13
ΔE (kJ/mol)	5.66	5.07	6.29	12.74

Table 5 Assessment of Cr(VI) removal capabilities using multiple adsorbents

Adsorbent	Synthesis Method	S_a (m ² /g)	pH	T(K)	Dose (g/L)	Time (min)	Cr (VI) (mg/L)	q_{max} (mg/g)	Ref.
Algae magnetic AC	Pyrolysis	-	3	-	1	90	20 to 60	15.24	(Afshin et al., 2021)
<i>Peganum harmala</i> seeds AC	Ultrasonication	442.98	3	298	10	80	20 to 200	16.66	(Nasseh et al., 2021)
nFe ₂ O ₃ @AC	Pyrolysis plus Co-precipitation	724	3	298	0.25	720	5 to 500	32.1	(Li et al., 2019)
Typha MAC	Pyrolysis	52.64	6	298	1	720	25 to 125	55.5	(Cai et al., 2024)
Termite feces magnetic AC	Pyrolysis	699	4	298	0.5	240	25 to 200	66	(Demar-chi et al., 2019)
Sludge based magnetic AC	Pyrolysis plus co-precipitation	119.56	2	300	5	240	25 to 100	80.21	(Ramya et al., 2022)
Mushroom magnetic AC	Pyrolysis	782.64	1	303	1	120	3 to 20	100.94	(Pan et al., 2025)
Phosphoric acid treated Af-MAC	Pyrolysis plus co-precipitation	472.98	2	303	0.25	180	5 to 25	114.09	This study

3.2.5 Assessment of Af–MAC regeneration

The Af–MAC regeneration potential for Cr(VI) removal was assessed over five cycles using 0.1 M NaOH as the regenerating agent (Fig. 8a). Initially, Af–MAC demonstrated excellent performance, achieving a Cr(VI) adsorption of 99.75% with an adsorption capacity of 19.95 mg/g. However, with each successive cycle, a gradual decline in both Cr(VI) uptake potential and adsorption capacity was observed. By the second cycle, the uptake efficiency had declined to 96.12%, and the adsorption capacity dropped to 19.22 mg/g. This trend continued through the third and fourth cycles, where the removal efficiencies were 88.93 and 78.86%, and the adsorption capacities were 17.79 mg/g and 15.77 mg/g, respectively. The fifth cycle exhibited the most significant reduction, with the removal efficiency falling to 64.90% and the adsorption capacity declining to 12.98 mg/g. The observed decline in Af–MAC's performance is likely because of the loss of active binding sites, pore blockage, and formation of surface complexation, which impede the adsorption process (Vinayagam et al., 2023), (Patra et al., 2020). This suggests that Af–MAC is effective for Cr(VI) removal, making it suitable for up to four cycles.

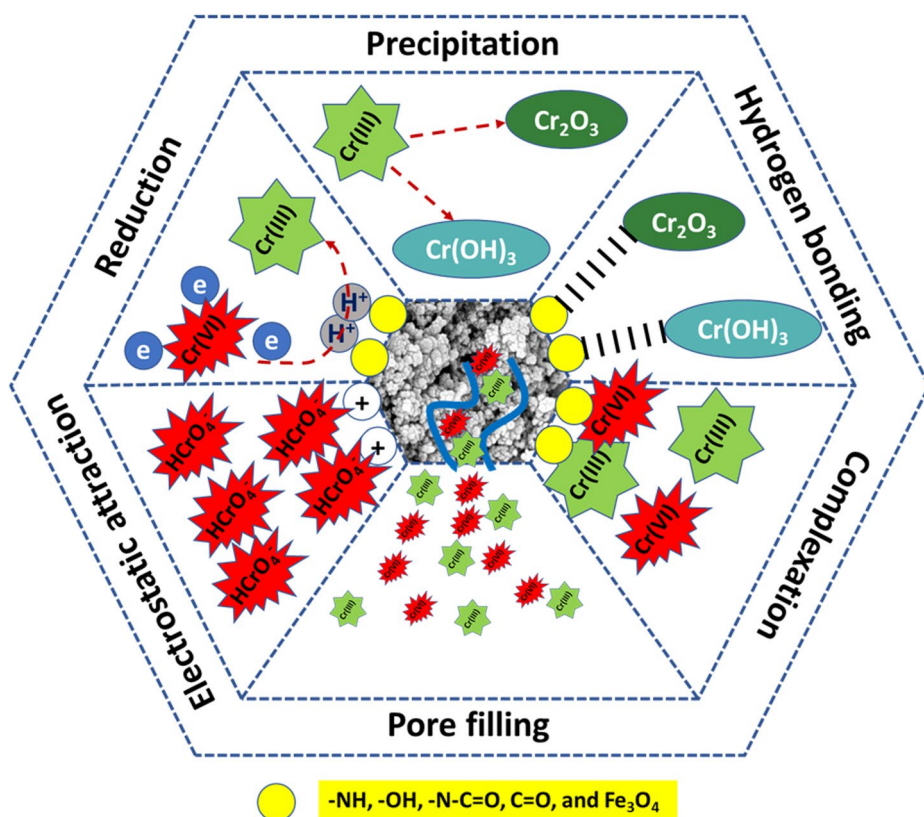


Fig. 7 Proposed Cr(VI) removal mechanism employing Af-MAC as adsorbent

3.2.6 Impact of competing ions in aqueous solutions on Cr(VI) adsorption

The effect of various cations and anions on Cr(VI) removal utilizing Af-MAC was studied, with findings detailed in Fig. 8b. In distilled water (DW), Af-MAC achieved Cr(VI) adsorption of 99.75% with an adsorption capacity of 19.95 mg/g. The introduction of cations like K^+ , Na^+ , and Ca^{2+} led to slight decreases in removal efficiency (Zheng et al., 2021), (ranging from 97.89 to 98.20%) and adsorption capacity (from 19.58 to 19.64 mg/g). Among these, Ca^{2+} ions can interact with negatively charged Cr(VI) species in the aqueous solution, forming ion pairs. This interaction can effectively shield the negative charge of the chromium species, potentially reducing their electrostatic attraction to the positively charged active sites on the Af-MAC surface.

Anions had a more significant effect, with sulfate (SO_4^{2-}) reducing the removal efficiency to 85.21% and nitrate (NO_3^-), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}) further lowering it to 75.32%, 68.95%, and 71.40%, respectively. The significant reduction in performance in the presence of these anions is likely due to their strong competition with Cr(VI) for adsorption sites on Af-MAC, as well as potential interactions that reduce the availability of Cr(VI) for adsorption (Zheng et al., 2021), (Flores et al., 2024).

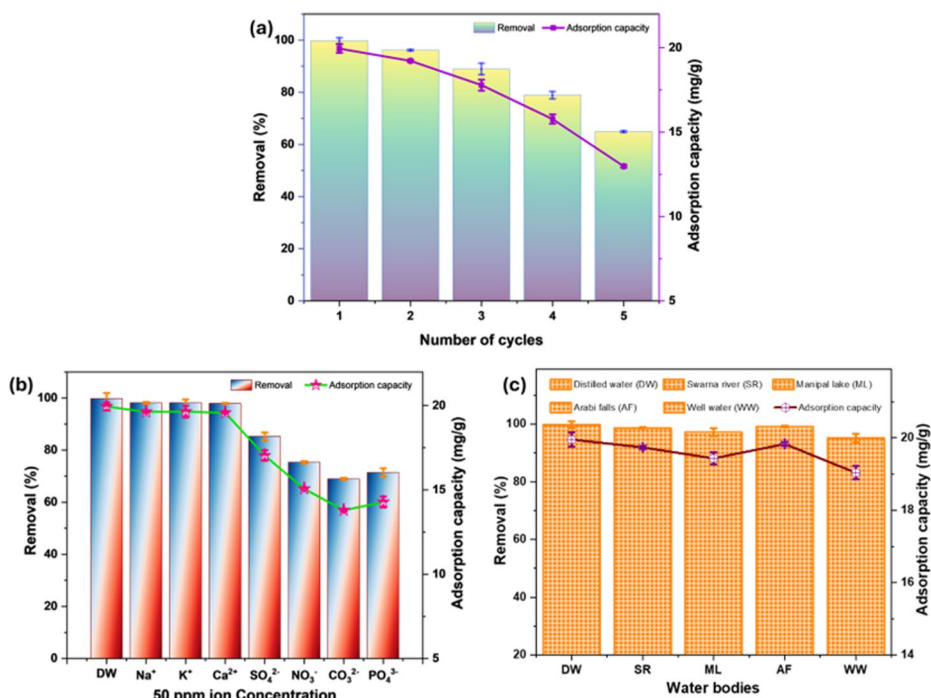


Fig. 8 Regeneration potential of Af-MAC using NaOH (a), effect of co-existing ions (b), and effect of interfering species present in real water (c), for Cr(VI) adsorption

3.2.7 Evaluation of Af-MAC efficiency to adsorb Cr(VI) from spiked samples

Af-MAC potential to remove Cr(VI) was evaluated by spiking studies in diverse water bodies. As shown in Fig. 8c, Af-MAC demonstrated 99.78% efficiency and an adsorption capacity of 19.96 mg/g in distilled water, indicating optimal performance. In the Swarna river water, the removal performance decreased slightly to 98.68% (19.74 mg/g), likely because of competing substances or organic matter in the river. The removal performance further declined in Manipal Lake water to 97.17% (19.43 mg/g), potentially due to additional contaminants or variations in lake water chemistry. Af-MAC performed well in Arabi Falls water, achieving a removal of 99.16% and an adsorption capacity of 19.83 mg/g, suggesting minimal interference from water constituents. The lowest performance was observed in well water, with 95.19% (19.04 mg/g), possibly due to high concentrations of natural organic matter or minerals. These findings suggest the promising potential of Af-MAC to be used in remediation strategies for Cr(VI) adsorption.

4 Conclusions

This research work demonstrates that Af-MAC is an effective and sustainable material for Cr(VI) removal. Structural and chemical characterizations (XRD, FESEM, EDS, VSM, XPS, FTIR) confirmed strong interactions between surface functional groups and Cr(VI),

while embedded Fe_3O_4 nanoparticles enhanced adsorption performance and enabled facile magnetic separation.

Implications to theory and practice:

The adsorption behavior of Af–MAC, particularly its optimal performance at acidic pH due to surface protonation, aligns with established adsorption theory, where electrostatic attraction governs the uptake of anionic species. The statistical physics model (TLOE) revealed parallel binding of Cr(VI) with an adsorption capacity of 114.09 mg/g at 303 K, supporting the predominance of physisorption ($\Delta E < 15$ kJ/mol). From a practical perspective, Af–MAC combines high adsorption efficiency with magnetic recovery, positioning it as a low-cost and operationally feasible alternative for Cr(VI) removal in real wastewater systems.

Key lessons learnt:

This work highlights that phosphorus modification and magnetic incorporation significantly enhance the adsorption capacity and reusability of biomass-derived carbons. While cations showed minimal interference, competing anions reduced Cr(VI) uptake, underscoring the need to account for real-water matrix effects. Regeneration studies further revealed that Af–MAC can be reused for up to four cycles with greater than 78% efficiency, balancing performance with sustainability.

Limitations of this study:

Despite its promising performance, certain limitations remain. Regeneration efficiency decreased after successive cycles because of pore clogging and loss of active surface sites, and chromium complexation. Furthermore, the experiments were primarily conducted in controlled batch systems, which may not fully represent the complexity of real wastewater. Future studies should focus on scaling up to continuous flow systems, testing with diverse industrial effluents, and exploring strategies to enhance the long-term stability and regeneration efficiency of Af–MAC.

Overall, Af–MAC combines high surface area, mesoporosity, magnetic properties, and regeneration potential, demonstrating its promise as a sustainable Cr(VI) adsorbent.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal. The authors affirm that this research was carried out independently and did not receive any financial assistance, funding, or sponsorship from governmental, industrial, or private organizations.

Data availability All relevant data can be obtained from the authors upon request.

Declarations

Generative AI and AI-assisted technologies in the writing process The authors used ChatGPT to check grammar and refine sentences, after which they reviewed and edited the content and took full responsibility for the final manuscript.

Consent for publication Not applicable.

Ethics approval This study does not contain any studies with human or animal subjects performed by any of the authors.

Consent to participate Not applicable.

Conflicts of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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