

Surface characterization and adsorption mechanism of carboxymethyl cellulose for cadmium(II) removal from aqueous solution

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ABSTRACT

A comprehensive analytical investigation was undertaken into the mechanistic process behind the adsorption of cadmium (II) onto the carboxymethyl cellulose (CMC) using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), equilibrium isotherm modeling, and adsorption kinetic analysis. The batch experiments were done under the previously optimized conditions (contact time = 50 min, pH = 6, T = 25 °C, C₀ = 20 mg/L, adsorbent dose = 1 g/L), at which the reference removal efficiency was 88%, and the equilibrium adsorption capacity was 17.6 mg/g. FTIR studies showed that the adsorption of Cd(II) led to a characteristic shift of the asymmetric (–COO[–]) stretching band from 1622.13 to 1608.63 cm^{–1}, which is consistent with surface complexation between Cd(II) and the carboxymethyl functional groups of CMC. The presence of new sharp diffraction peaks in the XRD spectra of the Cd(II) loaded CMC was indicative of deposition of crystalline cadmium-containing phases over the adsorbent surface, and the SEM images showed a significant morphological change from an open fibrous network to a close-packed lamellar structure with near-cubic crystalline surface deposits. The Freundlich isotherm (R² = 0.997, and RMSE = 0.612 mg/g) was the best model to define the equilibrium data, while the Langmuir model yielding a theoretical maximum monolayer adsorption capacity of q_{max} = 35.0 mg/g and separation factor R_L = 0.091, indicating favorable adsorption within the Langmuir model framework. The pseudo-second-order model best fit the data gotten from kinetic analysis, with R² = 0.998 and (q_e)_{cal} = 18.87 mg/g, which indicates that is consistent with a chemisorption-dominated mechanism and is consistent with the FTIR mechanistic evidence. A non-zero intraparticle diffusion intercept confirmed the multi-step rate control that included film and pore diffusion. Convergent evidence of all the characterization and modeling methods confirms that CMC is a well-defined, mechanistically effective, and biodegradable adsorbent, as reported in the literature, for the remediation of Cd(II) in contaminated water systems.

Keywords: carboxymethyl cellulose, cadmium (II) adsorption, heavy metal remediation, surface characterization, aqueous solution, wastewater treatment.

INTRODUCTION

Among highly hazardous heavy metals found in polluted water systems is cadmium (Cd), due to its environmental persistence, high bioaccumulation potential, and drastic toxicological effects to life forms. However, chronic exposures at low concentrations have been causally associated with renal tubular dysfunction, skeletal fragility,

and hepatic injury. This has led the World Health Organization to recommend a maximum permissible concentration of 0.003 mg/L in drinking water (Singh et al., 2022). The industrial activities producing phosphate fertilizers, electroplating, and batteries continue to be the primary Cd sources in surface and groundwater bodies, highlighting the need for efficient and affordable remediation measures (Al-Khuzai et al., 2024).

Conventional technologies, comprising chemical precipitation, ion exchange, and membrane filtration, have been well documented to have certain disadvantages, including the cost of operation, sludge creation, and low performance at low metal concentrations (Velarde et al., 2023). Thus, adsorption has remained an active research field as an alternative method that is easily applied, inexpensive, and highly scalable. The use of adsorbents made from biopolymers has witnessed a rapid growth, due to the growing demand for biodegradable and environmentally friendly materials that can be sourced from renewable resources in this area (Okoro et al., 2022). Carboxymethyl cellulose (CMC) is an anionic derivative of native cellulose, where the hydroxyl hydrogen atoms of the polysaccharide backbone are replaced by a controlled introduction of the carboxymethyl group ($-\text{CH}_2\text{COOH}$) (Rahman et al., 2021). After deprotonation at near-neutral pH levels, the CMC surface is highly anionic, featuring ionized carboxylic groups ($-\text{COO}^-$) that can be applied for strong electrostatic binding and surface coordination of heavy metal ions such as Cd(II) (Zhang et al., 2024). Based on the above chemical properties, CMC's biodegradability, non-toxicity, and commercial availability, properties well-documented in the literature (Rahman et al., 2021), position it as a technically and environmentally promising adsorbent for the removal of heavy metals. A complete surface characterization of the adsorbent material is a crucial component of any adsorption mechanistic study, done both prior to and following the uptake of adsorbate metal. The direct involvement of functional groups in Cd(II) binding by the change in the characteristic absorption bands is viewed in Fourier transform infrared spectroscopy (FTIR), and the crystal structure of CMC is found to change upon interaction with Cd(II) metal by X-ray diffraction (XRD) study (Sh. Ajeel et al., 2026). scanning electron microscopy (SEM) showed some detailed morphological and elemental evidence showing that the cadmium was deposited on the adsorbent's surface after adsorption (Khalaf et al., 2025). Equilibrium isotherm and kinetic analyses are equally important, providing insights into the adsorbent surface's characteristics, the maximum adsorption capacity, and the rate-controlling mechanism underlying the uptake of metals, which are crucial for rational process design and engineering scale-up (Ali et al., 2024).

The design of this research was done to reveal the adsorption mechanism of Cd(II) on CMC beyond the parametric performance based on the optimal batch conditions found in the previous research, which were adsorbent dose 1.0 g/L, contact time 50 min, pH 6, and initial Cd(II) concentration 20 mg/L at 25 °C with 88% removal efficiency and 17.6 mg/g equilibrium adsorption capacity. The scientific novelty of the present study stems from two complementary aspects. First, this study provides the first mechanistic characterization of Cd(II) adsorption onto unmodified commercial sodium CMC through an integrated multi-technique analytical approach combining FTIR, XRD, and SEM. Furthermore, the present study constitutes the second part of a systematic research series, progressing from optimization both of the operational and environmental conditions (Part I) to comprehensive mechanistic characterization (Part II). Collectively, this integrated approach establishes a stronger scientific basis for the application of CMC without any processing in the treatment of heavy-metal-contaminated wastewater. This study aimed specifically to (i) define the adsorption equilibrium utilizing Freundlich, Temkin, and Langmuir isotherm models; (ii) elucidate the rate-controlling mechanism utilizing pseudo second-order, intraparticle diffusion kinetic, and pseudo first-order models; (iii) characterize the physicochemical properties of the CMC surface before and after Cd^{2+} adsorption utilizing FTIR spectroscopy, SEM and XRD; and (iv) provide a mechanistically coherent, yet experimentally based account of Cd(II) uptake by CMC for its use in the removal of heavy metal from wastewater.

MATERIALS AND METHODS

Chemicals and reagents

As the adsorbent material, carboxymethyl cellulose sodium salt, CMC (Sigma-Aldrich, Germany) was used, with a degree of substitution value DS (0.7–1.2). The preparation of a stock solution of Cd(II) (1000 mg/L) in deionized water was done using a known and accurate weight of the analytical grade cadmium nitrate tetrahydrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck Germany, $\geq 98\%$ purity] and freshly prepared by serial dilution prior to each experiment. By adding 0.1 mol/L NaOH or 0.1 mol/L HCl (BDH Chemicals, United

Kingdom) and verified using a calibrated pH meter, the adjustment of pH of the solutions was completed. The pH of the solution was checked at the end of each experiment and was found not to have deviated from the initial value by more than ± 0.3 pH units.

Adsorbent preparation

The CMC sodium salt used for this investigation was physically conditioned in a convection oven for 12 hours at 60 °C to remove moisture from the atmosphere to ensure gravimetric accuracy in the subsequent investigation procedures, as done by Ali et al. (2024). The dried material after thermal treatment, underwent size-reduction to break the agglomerates and increase the free-flow of the particles in the porcelain mortar and pestle (Figure 1), and to obtain a more uniform particle size distribution after size-reduction of the pre-ground powder in a laboratory ball mill (Khalaf et al., 2025). The milled product was then fractionated by passing through a series of calibrated stainless-steel sieves to obtain a homogeneous particle size fraction of the range 100–250 μm , which is necessary in adsorption work to reduce inter-experimental variations due to differences in external surface area and the solid–liquid mass transfer resistance. The size-fractionated CMC powder was



Figure 1. Manual grinding of dried CMC powder using a porcelain mortar and pestle as a preliminary size-reduction step prior to mechanical milling

finally sealed in airtight glass containers and stored under desiccated conditions at ambient temperature, protected from humidity and light exposure, until required for characterization and adsorption experiments (Sh. Ajeel et al., 2026).

Physicochemical characterization

The CMC adsorbent's surface chemistry and morphology were examined before and after Cd(II) adsorption using three complementary analytical techniques. On a Shimadzu FTIR spectrometer over the range 400–4000 cm^{-1} , infrared spectra were recorded to recognize the functional groups that participated in metal binding and to detect any spectral shifts induced by Cd(II) coordination (Sh. Ajeel et al., 2026). By X-ray powder diffraction, the crystalline structure was examined utilizing Cu-K α radiation ($\lambda = 1.5406$ Å) over a 2θ range of 5°–95°, with pre- and post-adsorption diffractograms compared to assess structural modifications arising from metal uptake. The CMC's surface morphology was evaluated utilizing scanning electron microscopy at 500 $\times$ magnification and 30 kV accelerating voltage (College of Engineering, Tikrit University) to directly compare the surface texture of the CMC before and after Cd(II) adsorption (Pushpamalar et al., 2006; Churam et al., 2024).

Batch adsorption experiments

In batch mode, the tests of adsorption were performed using the parameters optimized in the previous experiments as follows: pH value was 6, initial Cd(II) concentration (C_0) was 20 mg/L, with 25 °C temperature, 50 min contact time, 1 g/L adsorbent dose (M), and 150 rpm agitation speed in continuous mode. The suspension was filtered at the end of each experiment through a filter with a 0.45 μm membrane. The measurement of remaining Cd(II) content in the clarified filtrate was taken at $\lambda = 228.8$ nm utilizing a UV-Visible spectrophotometer (HACH DR6000, Germany) according to the standard methods (Ali et al., 2024). The calculation of the equilibrium adsorption capacity (q_e , mg/g), and removal efficiency ($R\%$) was done using:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_t \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_t)}{W} \times V \quad (2)$$

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_e)}{W} \times V \quad (3)$$

The dry adsorbent mass is denoted by W (g), where C_0 (mg/L) is the initial Cd^{2+} concentration, C_t (mg/L) is the concentration at time t , the equilibrium Cd(II) concentration is denoted by C_e (mg/L), and the solution volume is denoted by V (L). Experiments were done in triplicate, and the mean values $\pm$ standard deviation are employed to report the results (Agarwal et al., 2026).

Adsorption isotherm models

To explore the equilibrium adsorption data, the Temkin, Langmuir, and Freundlich isotherm models were utilized.

Monolayer adsorption on a homogeneous surface with the same binding spots is described by the Langmuir model (Foo and Hameed, 2010):

$$q_e = \frac{q_{\text{max}} \times b \times C_e}{1 + b \times C_e} \quad (4)$$

The theoretical maximum adsorption capacity is denoted by q_{max} (mg/g), and the affinity constant is denoted by b (L/mg). The Freundlich model addresses multilayer adsorption on energetically heterogeneous surfaces:

$$q_e = k_f \times C_e^{1/n} \quad (5)$$

The capacity coefficient is denoted by K_p , and n is the heterogeneity factor; values of $n > 1$ denote favorable adsorption conditions (Wang et al., 2017).

In adsorption heat with surface coverage, the Temkin model acts a linear decline reflecting adsorbent–adsorbate interaction energies:

$$q_e = B \times \ln(AT \times C_e) \quad (6)$$

The heat of adsorption is denoted by B (J/g). The equilibrium binding constant is denoted by AT (L/g). With model selection based on the coefficient of determination (R^2), and the root mean square error (RMSE) (Equation 7), model parameters were determined by linear regression. Linear models were adopted in this study for the following methodological reason: they enable direct comparison with the majority of studies in the scientific literature that follow the same approach, thereby facilitating the placement of the results within the appropriate reference context.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n [(q_e)_{\text{exp}} - (q_e)_{\text{cal}}]^2} \quad (7)$$

Adsorption kinetic models

The kinetics of Cd(II) adsorption onto CMC were examined using three established models to identify the mechanism that controls the rate of metal uptake. It is believed that the quantity of available surface locations determines the adsorption rate in the pseudo-first-order (PFO) model (Qiu et al., 2009):

$$q_t = q_e \times (1 - e^{-k_1 \times t}) \quad (8)$$

At time t , the adsorption capacity is denoted by q_t (mg/g). k_1 (min^{-1}) denotes the PFO rate constant, and the equilibrium capacity is represented by q_e (mg/g).

The pseudo-second-order (PSO) model presupposes that chemisorption, implying electron exchange or sharing between Cd^{2+} ions and CMC surface functional groups, constitutes the rate-limiting step (Foo and Hameed, 2010):

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (9)$$

The PSO rate constant is denoted by k_2 (g/mg.min). Agreement between the calculated q_e and the experimental value is a prerequisite for accepting this model. The intraparticle diffusion (IPD) model of Morris and Weber was used to assess whether pore diffusion constitutes a rate-limiting step:

$$q_t = k_p \times t^{0.5} + C \quad (10)$$

The intercept reflecting the boundary layer thickness is denoted by C (mg/g), and the intraparticle diffusion rate constant is denoted by k_p (mg/g.min^{0.5}). A non-zero intercept indicates that both intraparticle diffusion and external film diffusion have an impact on the total adsorption rate. The model was chosen based on the convergence between $(q_e)_{\text{exp}}$ and $(q_e)_{\text{cal}}$, as well as the coefficient of determination (R^2).

RESULTS AND DISCUSSION

Optimization of the adsorption conditions

Before the characterization and modeling investigations reported herein, a systematic parametric optimization of Cd(II) adsorption onto CMC was conducted under batch equilibrium conditions. The best operating conditions for Cd(II) removal were determined to be as follows: initial Cd(II) concentration = 20 mg L⁻¹, pH = 6, temperature =

25 °C, contact time = 50 min, and adsorbent dose = 1.0 g L⁻¹, at which the maximum Cd(II) removal efficiency of 88% and maximum adsorption capacity at equilibrium of 17.6 mg g⁻¹ were obtained. The above conditions were taken as the reference conditions for all the characterization and modeling experiments presented hereafter.

FTIR spectroscopic analysis

Before and after adsorption of Cd(II) ions (400–4000 cm⁻¹ wavenumber range), FTIR spectra of CMC were obtained with a Shimadzu FTIR spectrometer (Figure 2). The spectrum of virgin CMC presented an extensive absorption band at 3425.58 cm⁻¹, which is reported as a diagnostic band of polysaccharide matrices and is a result of

O–H stretching vibrations, participating in an inter and intramolecular hydrogen bonding network. The band at 2924.09 cm⁻¹ is attributed to asymmetric C–H extending from the anhydroglucose backbone, and the most analytically significant band is the prominent absorption at 1622.13 cm⁻¹, which is attributed to asymmetric stretching of ionized carboxylate groups (–COO⁻), which are the principal functional groups responsible for metal cation complexation in CMC (Churam et al., 2024). It is well known that the range of 1588–1622 cm⁻¹ and 1413–1423 cm⁻¹ are characteristic of the appearance of carboxymethyl groups and their sodium salts, respectively, indicating materials of carboxymethyl cellulose. Absorptions at 1265.30, 1155.36, and 1053.13 cm⁻¹ were attributed to C–O–C glycosidic linkage, C–O extending,

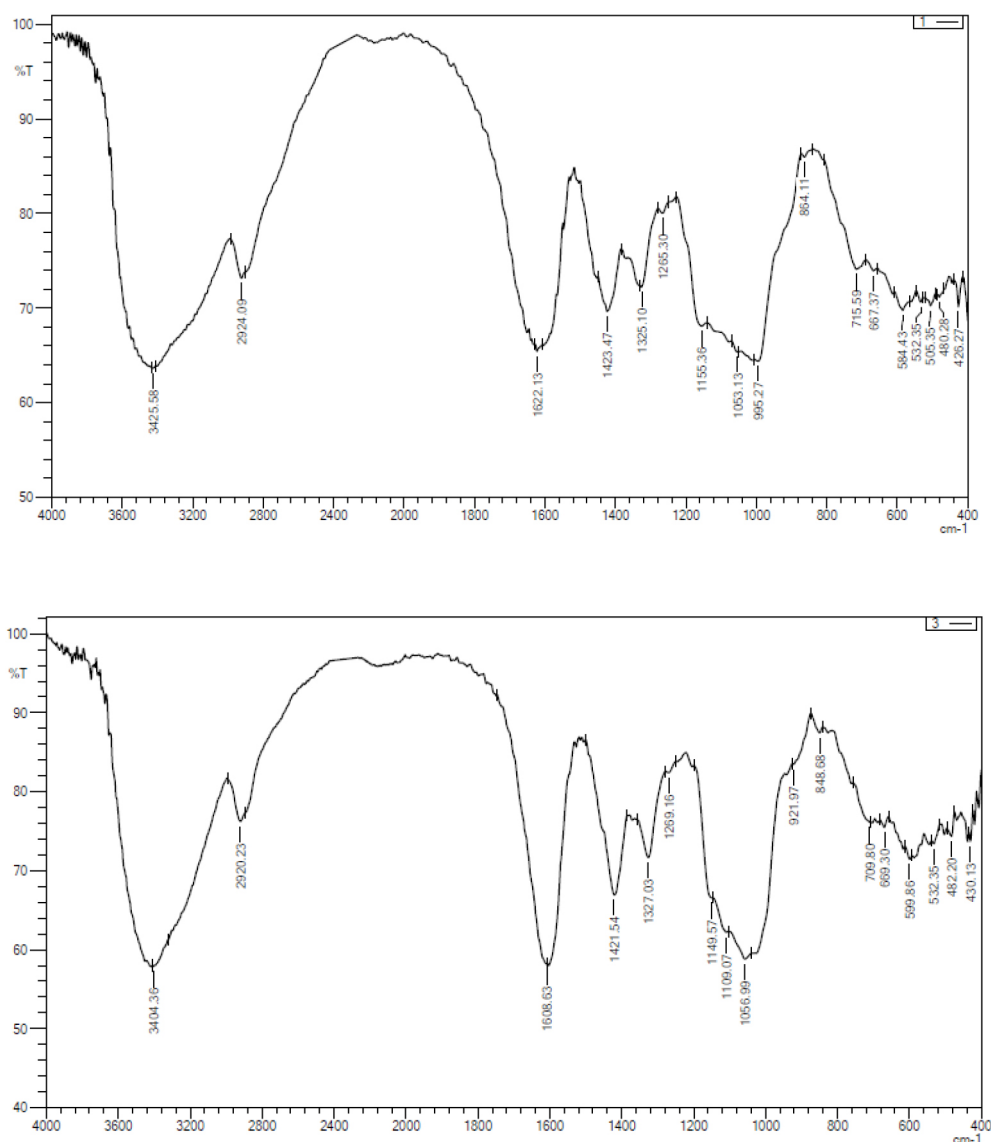


Figure 2. FTIR spectra of CMC before (upper) and after (lower) Cd(II) adsorption; 400–4000 cm⁻¹ wavenumber range

and C–OH stretching, respectively, which indicated the integrity of the polysaccharide backbone (Liu et al., 2025). After the adsorption of Cd(II), a number of spectral changes of mechanistic importance were noted (Figure 2). The O–H stretching band was red-shifted by 21.2 cm^{-1} from 3425.58 cm^{-1} to 3404.36 cm^{-1} in the metal ion's presence, which shows the effect of the perturbation of the hydrogen bonding network upon the coordination of the metal ion. Most importantly, the asymmetric ($-\text{COO}^-$) stretching band experienced a red shift of 14 cm^{-1} from 1622.13 cm^{-1} to 1608.63 cm^{-1} , which is consistent with surface complexation between Cd(II) cations with CMC's carboxylate groups (Shakil et al., 2024). In general, changes in the carboxylate stretching region after the adsorption of the metal ion on CMC-based materials are attributed to electrostatic coordination and surface complexation between divalent metal cations and the ($-\text{COO}^-$) functional groups. A shift in C–O–C glycosidic band ($1155.36 \rightarrow 1149.57\text{ cm}^{-1}$) and C–OH stretching ($1053.13 \rightarrow 1056.99\text{ cm}^{-1}$) further points to the participation of the hydroxyl groups as secondary interactions in the binding of Cd(II) (Zhang et al., 2024). A 1109.07 cm^{-1} band is absent in the post-adsorption spectrum, suggesting the structural rearrangement of the CMC chain after metal coordination. All the spectral changes indicate that ($-\text{COO}^-$) groups are the main active site points that control the adsorption of Cd(II) on CMC (Pang et al., 2022). While the convergent spectroscopic, crystallographic, morphological, and kinetic evidence presented herein strongly supports a surface complexation mechanism involving the ($-\text{COO}^-$) functional groups of CMC, definitive assignment of inner-sphere versus outer-sphere coordination would require complementary techniques such as EXAFS spectroscopy, which is recommended for future investigation.

X-Ray diffraction characterization

The XRD diffractograms of CMC before and after the adsorption of Cd(II) are illustrated in Figure 3. The virgin CMC pattern revealed a single broad, diffuse reflection at $2\theta \approx 22^\circ$, which is the crystallographic signature for the semi-crystalline structure of sodium carboxymethyl cellulose that results from the partial disruption of the ordered hydrogen bonding network of native cellulose during the carboxymethylation process of hydroxyl groups (Liu et al., 2025). The lack of sharp and well-resolved diffraction peaks

throughout the rest of the scan range indicates the predominantly amorphous nature of the material, which is beneficial for adsorption purposes as it suggests a higher accessibility and mobility of the surface functional groups to the incoming metal ions in solution (Zhang et al., 2024). After Cd(II) adsorption, significant changes in the diffractogram were observed, indicative of clear crystallographic evidence of successful metal uptake on the CMC surface (Figure 3). The general reflection at $2\theta \sim 20\text{--}21^\circ$, typical of the CMC matrix, was not lost, but a discernible decrease in its peak intensity and a slight shift towards lower diffraction angles were noted. This can be explained by the disruption of the residual ordered domains in CMC after the coordination of Cd(II) with $-\text{COO}^-$ groups, which leads to a higher proportion of the amorphous state of the Cd(II) loaded adsorbent (Pan et al., 2025). Specifically, several prominent diffraction peaks, which were all missing in the virgin CMC pattern, appeared at 2θ values of $\sim 32^\circ$, 47° , 57° , 66° , 75° , and 80° , respectively. These new reflections are tentatively attributed to possible Cd-containing crystalline phases, which deposit on the adsorbent surface after the metal uptake from the solution (Rodríguez et al., 2025). It is pertinent to note that all adsorption experiments were conducted at pH 6, which lies well below the thermodynamic precipitation threshold of $\text{Cd}(\text{OH})_2$ ($\text{pH} > 8\text{--}9$), thereby excluding bulk precipitation as a contributing removal mechanism under the experimental conditions adopted. It is acknowledged, however, that no control experiment without CMC was conducted, and such a control is recommended for future investigations. These results agree with the FTIR results reported in Section 3.2, and together, they demonstrate that the Cd(II) removal onto CMC is not by non-specific physical retention but by genuine surface chemical interaction.

Scanning electron microscopy characterization

The CMC's surface morphology before and after Cd(II) adsorption was studied at $500\times$. Figure 4 exhibits representative micrographs. The SEM images shown of the virgin CMC (upper) reveal a markedly heterogeneous surface architecture, with the elongated fibrous units having curvilinear profiles and irregular cross sections and being arranged in an entangled, loosely packed network with wide inter-fiber voids and open macropores.

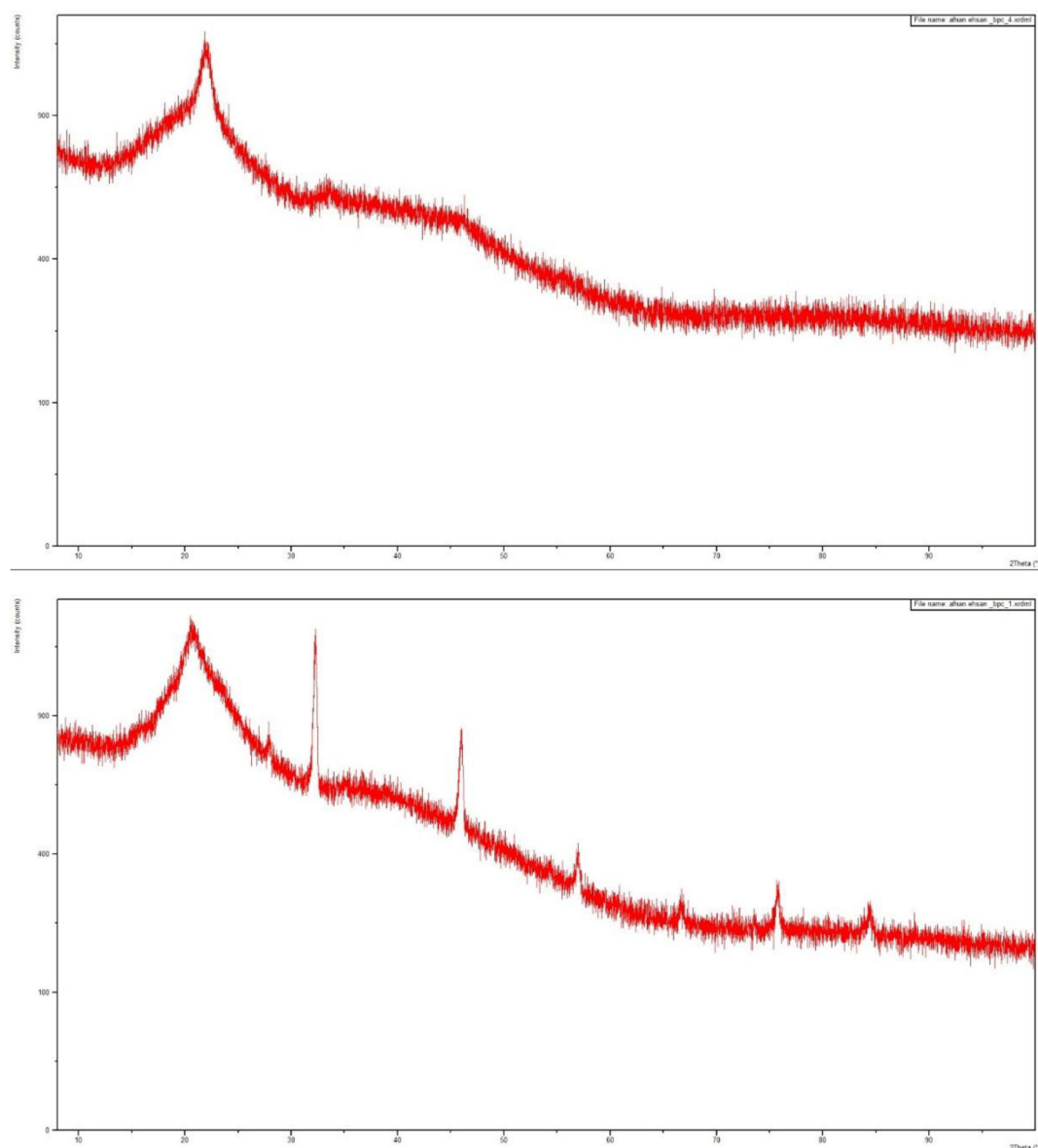


Figure 3. XRD diffractograms of CMC before (upper) and after (lower) Cd(II) adsorption.
Instrument: X-ray diffractometer, 2θ range: 5° – 95° ; Cu- $K\alpha$ radiation

The surfaces of each individual fiber are rough and topographically varied at $500\times$ magnification (lower), with the presence of angular and near-cubic microparticulate deposits across the fiber exteriors, attributed to residual surface irregularities that result from the two-stage mechanical size reduction protocol during adsorbent preparation (Capanema et al., 2018). The huge external surface area of this open and porous structural configuration is particularly significant in functional terms as it allows the Cd(II) ions to diffuse to reach the $(-\text{COO}^-)$ active sites found along the biopolymer chains (Anene and Nwokoye, 2026). The morphology of the fibers observed in this study aligns with the semi-crystalline, partially

amorphous nature of CMC, confirmed through XRD analysis in Section 3.3, where the structural disorder at the polymer chain level is reflected at the microscopic scale as surface roughness (Churam et al., 2024). After adsorption of Cd(II), a visually unambiguous and structurally decisive change of the CMC surface appeared. The once-open and entangled fibrous network was completely replaced with a completely different macrostructure with a large, flat, lamellar shape; smooth planar surfaces; and neat layered stacking, which means a transition from a fibrous to a sheet-like texture of the CMC matrix as a result of the incorporation of the metal (Pan et al., 2025). The presence of voids between fibers seen

in virgin CMC was significantly reduced, and the general surface was denser and more compact. The presence of prominent near-cubic crystalline deposits on the post-adsorption surface is easily detected, and their location and shape are fully consistent with the new sharp diffraction reflections observed in the XRD pattern of Cd(II) loaded CMC that were tentatively attributed to possible Cd-containing crystalline phases, the precise identification of which would require systematic matching against standard reference diffraction patterns (ICDD/PDF database). This morphological densification is, mechanistically, thought to be due to the progressive increase of the concentration of Cd(II) ions, which occupy ($-\text{COO}^-$) surface binding sites, inducing, by cadmium–carboxylate complex formation, inter-chain electrostatic bridging and, consequently, a decrease in the openness of the biopolymer matrix. Examples of such morphological consolidation after heavy metal uptake on adsorbents derived from CMC have been well documented in the recent literature, where the smoothing of the surface, the filling of the voids, and the presence of crystalline deposits as a whole are macroscopic markers of saturation of the active sites and successful metal sequestration (Liu et al., 2025). Considering the family of SEM images, they provide visual support consistent with the adsorption mechanism, based on FTIR spectroscopic evidence, based on XRD crystallographic evidence. It should be noted that elemental analysis using EDX/EDS was not performed in this study; consequently, the chemical identity of the observed surface deposits cannot be confirmed based solely on the morphological characteristics revealed by scanning electron microscopy (SEM). Therefore, conducting EDX analysis in future studies is recommended

to provide direct elemental evidence of cadmium (Cd) deposition on the CMC surface.

Adsorption equilibrium isotherm modeling

To explain the distribution of Cd(II) between the solution and CMC surface at equilibrium, the experiments were fitted to three generally applied isotherm models (Freundlich, Langmuir, and Temkin) using linear regression analysis. The ensuing fits are drawn in Figure 5. Table 1 shows the model parameters.

The theoretical maximum monolayer adsorption capacity (q_{max}) of the Langmuir isotherm is 35.0 mg/g, a coefficient of determination of $R^2 = 0.984$, and an affinity constant of $b = 0.50$ L/mg, which matched the experiments and confirmed that the adsorption of Cd(II) on CMC is favorable within the framework of the Langmuir model under the conditions studied (Anene and Nwokoye, 2026). The Langmuir model's applicability indicates that part of the adsorption procedure appears to be monolayer adsorption on homogenous binding sites, consistent with a uniform distribution of $-\text{COO}^-$ groups along the CMC backbone shown by FTIR analysis (Zhang et al., 2024).

Among the three models, the Freundlich isotherm provided the best statistical fit, yielding $R^2 = 0.997$, RMSE = 0.612 with a capacity coefficient $K_f = 13.07$ (mg/g) (L/mg) $^{1/n}$ and a heterogeneity factor $n = 3.10$. The value of $n > 1$ confirms that adsorption is favorable over the entire concentration range studied (Foo and Hameed, 2010). The Freundlich model was found to be more satisfactory than the Langmuir model, which matched the adsorption capacity that had not reached an apparent plateau in the investigated concentration range ($C_0 = 5\text{--}50$ mg/L). This indicates that

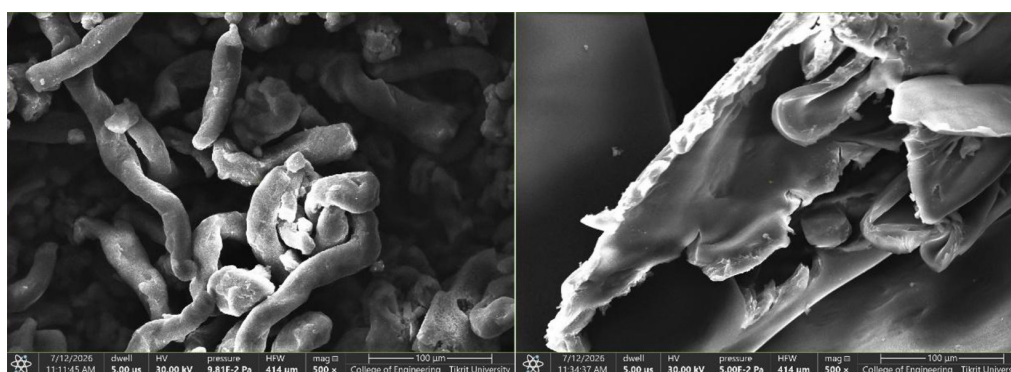


Figure 4. SEM micrographs of CMC: (left) before Cd^{2+} adsorption, 500 $\times$ showing entangled fibrous network with angular surface deposits; (right) after Cd(II) adsorption, 500 $\times$, showing lamellar compaction and near-cubic crystalline Cd-containing deposits. HV = 30.00 kV; scale bar = 100 μm

adsorption on a heterogeneous surface with a distribution of binding site energies is consistent with the overall adsorption behavior of Cd(II) and is consistent with the surface morphology of CMC, which is shown to be amorphous and porous based on SEM results (Pan et al., 2025).

The Temkin isotherm showed an acceptable fit ($R^2 = 0.973$), with a heat of adsorption parameter $B = 6.067$ J/g and an equilibrium binding constant $A_T = 9.51$ L/g. The positive B value indicates that the adsorption heat linearly declines with the surface coverage, which is the characteristic of chemisorption-type interaction on the heterogeneous surface of the adsorbent, where the interaction between the adsorbent and the adsorbate

weakens with the increase of surface coverage (Wang et al., 2017). Moreover, the Temkin constants are found to be in the moderate range of adsorbent–adsorbate interaction energies, which support the combined electrostatic and surface complexation mechanism and are proposed based on FTIR characterization (Kaur et al., 2022).

Adsorption equilibrium isotherm modeling

To determine the rate-controlling mechanism of Cd(II) adsorption onto CMC and to investigate the molecular-scale time-dependent adsorption behavior, the process kinetics were studied. The intraparticle diffusion (IPD), pseudo-first order

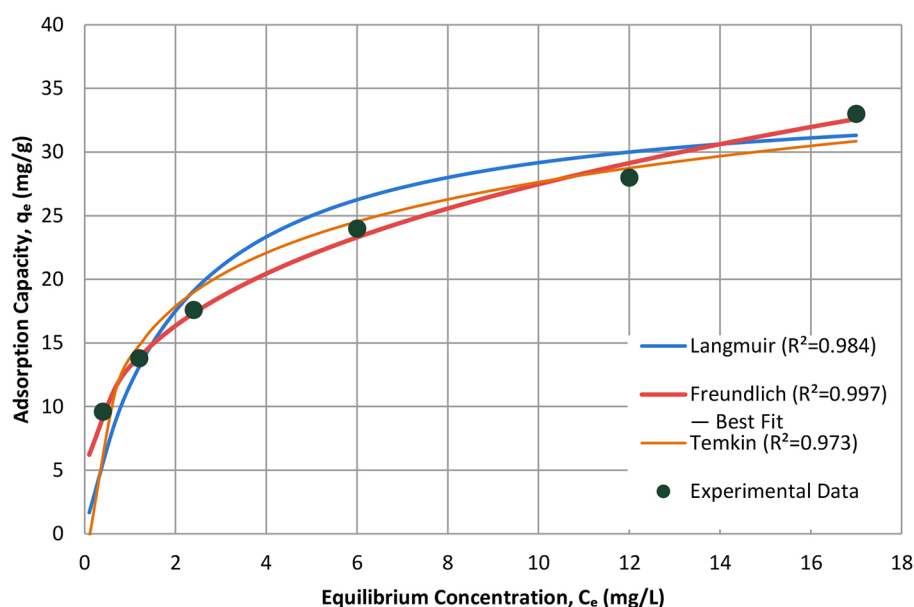


Figure 5. Temkin, Freundlich, and Langmuir isotherm models fit for Cd(II) adsorption onto CMC. Conditions: dose = 1 g/L; pH = 6; $t = 50$ min; agitation = 150 rpm; $T = 25$ °C

Table 1. Parameters of the adsorption isotherm model for Cd(II) adsorption onto CMC at pH 6, $T = 25$ °C

Isotherm model	Parameter	Value	Unit	R^2	RMSE (mg/g)	Interpretation
Langmuir	$q_{\max}$	35.0	mg/g	0.984	1.243	Maximum monolayer adsorption capacity
	b	0.50	L/mg			Langmuir affinity constant
	R_L	0.091	—			Separation factor: $0 < R_L < 1$ (favourable)
Freundlich	K_f	13.07	(mg/g) · (L/mg) ^{1/n}	0.997	0.612	Freundlich capacity coefficient
	n	3.10	—			Heterogeneity factor ($n > 1$ = favourable adsorption)
Temkin	B	6.067	J/g	0.973	1.587	Adsorption heat parameter ($B > 0$ = endothermic)
	A_t	9.51	L/g			Temkin equilibrium binding constant

Note: $R_L = 1 / (1 + b \times C_0) = 0.091$ at $C_0 = 20$ mg/L; $0 < R_L < 1$ indicates favourable adsorption within the Langmuir model framework. Best-fit model: Freundlich, ($R^2 = 0.997$), and (RMSE = 0.612).

(PFO), and pseudo-second order (PSO) models were used to fit the data of the experiments at q_t in the range 0–60 min, shown in Figure 6. Table 2 shows the derived kinetic parameters.

The PFO model gave $(q_e)_{cal} = 9.82$ mg/g and a rate constant of $k_1 = 0.0368$ min⁻¹ with a coefficient of determination of $R^2 = 0.981$. There was a reasonable statistical fit but a significant difference between $(q_e)_{cal}$ (9.82 mg/g) and the experimental data of $(q_e)_{exp}$ (17.6 mg/g), suggesting that the PFO model was inadequate to describe the real adsorption. This difference is usually explained to be caused by the model neglecting chemical interactions and the simplicity that the rate of adsorption varies only with the quantity of unoccupied surface sites (Qiu et al., 2009).

The PSO model, however, precisely associated with the experimental data ($R^2 = 0.998$) with a calculated value $(q_e)_{cal} = 18.87$ mg/g, which

matched the experimental value of 17.6 mg/g, and a second-order rate constant $k_2 = 0.0071$ g/mg.min (Foo and Hameed, 2010). In the PSO model, chemisorption is well-established as the rate-controlling stage in which either exchange or sharing of electrons occurs between the adsorbate ion and the active surface functional groups. The current model is strongly consistent with the spectroscopic evidence based on FTIR in Section 3.2 from which it was indicated that the cadmium–carboxylate complexes were formed at the surface of the CMC through surface coordination with the accompanied shift of the ($-\text{COO}^-$) asymmetric stretching band (1622.13 to 1608.63 cm⁻¹), though unambiguous confirmation of chemisorption as the sole rate-controlling step would require surface-sensitive spectroscopic techniques such as XPS or EXAFS analysis. Recent literature has widely confirmed the pseudo-second-order

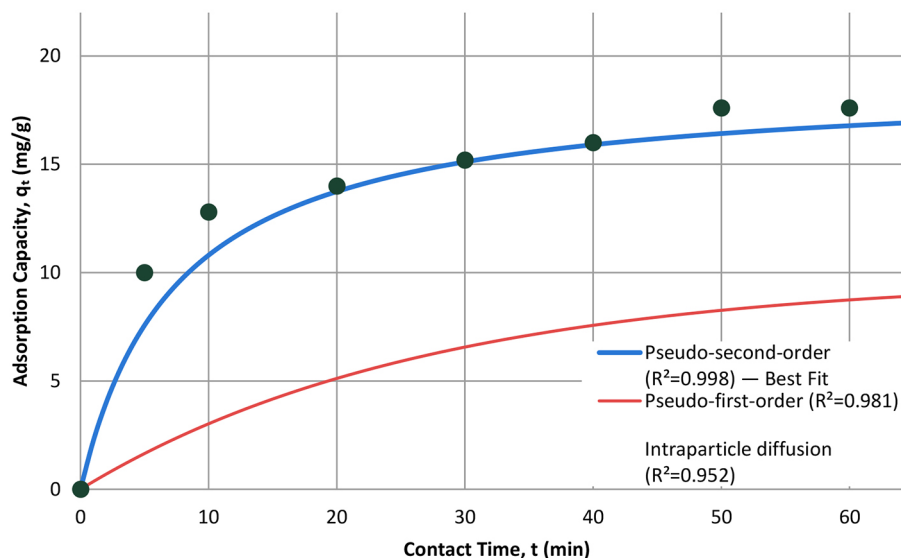


Figure 6. PFO, PSO, and intraparticle diffusion kinetic model fits for Cd(II) adsorption onto CMC. Conditions: $C_0 = 20$ mg/L; dose = 1 g/L; pH = 6; $T = 25$ °C; agitation = 150 rpm

Table 2. Kinetic model parameters for Cd(II) adsorption onto CMC

Kinetic model	Parameter	Value	Unit	R^2	Remark
Pseudo-first-order (PFO)	$(q_e)_{cal}$	9.82	mg/g	0.981	Poor fit — $(q_e)_{cal} \neq (q_e)_{exp}$
	K_1	0.0368	min ⁻¹		
Pseudo-second-order (PSO)	$(q_e)_{cal}$	18.87	mg/g	0.998	Best fit — chemisorption dominant
	K_2	0.0071	g/mg.min		
Intraparticle diffusion (IPD)	k_p	2.042	mg/g.min ^{1/2}	0.952	Multi-step rate control
	C	2.814	mg/g		$C \neq 0 \rightarrow$ film diffusion also controls
Experimental	$(q_e)_{cal}$	17.60	mg/g	—	Reference value for model comparison

Note: Conditions: $C_0 = 20$ mg/L; adsorbent dose = 1 g/L; pH = 6; $T = 25$ °C; $V = 100$ mL; agitation = 150 rpm. Best-fit model: Pseudo-second-order ($R^2 = 0.998$); $(q_e)_{cal} \approx (q_e)_{exp}$ confirms chemisorption mechanism.

nature of heavy metal adsorption systems involving CMC, with the rate-limiting interaction being electrostatic coordination between the polymer's carboxymethyl functional groups and the divalent metal cations (Zhang et al., 2024).

It was found that the intraparticle diffusion model of Weber and Morris gave a rate parameter, k_p , of 2.042 mg/g.min^{0.5} and a non-zero intercept, C , of 2.814 mg/g ($R^2 = 0.952$). The positive value of the C value indicates that surface adsorption and boundary layer (film) diffusion together regulate the total rate of Cd(II) removal by CMC, rather than intraparticle diffusion alone (Qiu et al., 2009). The multi-step kinetic behavior is associated with the complex hierarchical pore structure of the biopolymer-based adsorbents, where at the beginning of the process, the external film diffusion dominates the rapid uptake step, and in the final stage of adsorption, the intraparticle diffusion within the CMC matrix becomes more prominent (Wang et al., 2017).

CONCLUSIONS

In the current work, the Cd(II) adsorption onto carboxymethyl cellulose (CMC) has been mechanistically detailed using a multifaceted surface physical chemistry characterization, adsorption equilibrium isotherm modeling, and adsorption kinetic analysis. Based on the experimental and analytical results, the following major conclusions are presented.

FTIR spectroscopic analysis provided direct evidence at the molecule level that the carboxymethyl functional groups ($-\text{COO}^-$) of CMC are the main binding sites for the Cd(II) ions, as evidenced by the shift to lower wavenumber for the asymmetric stretching band of the ($-\text{COO}^-$) group from 1622.13 to 1608.63 cm^{-1} after adsorption, which is consistent with surface complexation between Cd(II) cations and the carboxylate groups of the biopolymer. The simultaneous changes in the OH and COC bands also designate the secondary role of hydroxyl groups in the coordination with the metal.

The virgin CMC showed a single broad reflection at $2\theta \approx 22^\circ$, indicating that the structure is predominantly amorphous by XRD analysis. The emergence of multiple new, sharp diffraction peaks in the diffractogram of the Cd(II) adsorbed CMC, which are lacking in the virgin CMC diffractogram, gave crystallographic evidence that the possible

Cd-containing crystalline phases were deposited on the surface of the adsorbent, the precise identification of which would require systematic matching against standard reference diffraction patterns (ICDD/PDF database), further supporting the surface chemical interaction mechanism proposed by FTIR analysis. SEM examination revealed a pronounced and visually unambiguous morphological transformation upon Cd(II) uptake, wherein the open, interconnected fibrous network of virgin CMC was replaced by a denser, more compact lamellar architecture with substantially reduced inter-fiber voids, accompanied by the appearance of near-cubic crystalline deposits consistent with the cadmium-containing phases identified by XRD.

As compared to the three isotherm models investigated, the Freundlich isotherm yielded the highest R^2 value (0.997), RMSE value (0.612), and best statistically represented the equilibrium data, indicating adsorption on a heterogeneous surface where a distribution of binding site energies exists. 35.0 mg/g theoretical maximum monolayer adsorption capacity and 0.091 dimensionless separation factor are provided by the Langmuir model, indicating favorable adsorption within the Langmuir model framework. The rate equation for the uptake of Cd(II) fitted well to the pseudo-second-order kinetic model ($R^2 = 0.998$). The q_e value was $(q_e)_{\text{cal}} = 18.87$ mg/g, which matched the experiments (17.6 mg/g), consistent with a chemisorption-dominated mechanism, which was also mechanistically supported by the FTIR results. Also, the non-zero intercept of the intraparticle diffusion model showed that the adsorption rate is influenced by the boundary layer diffusion.

Combined, the evidence from FTIR, XRD, SEM, isotherm, and kinetic analyses support a comprehensive and self-consistent mechanistic model for the adsorption of Cd(II) onto CMC, involving electrostatic attraction and surface complexation at carboxymethyl functional groups. The outcomes confirm the feasibility of cadmium removal utilizing CMC as an easily biodegradable, as reported in the literature, and cost-effective adsorbent whose mechanism has been well described.

Future studies are recommended to complement the current findings by employing elemental mapping (EDX) on the CMC surface following the adsorption process; this would provide direct elemental confirmation of cadmium ion Cd(II) deposition and reinforce the proposed adsorption mechanism.

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