

Study on the treatment of Cd(II) contaminated wastewater by multi-walled carbon nanotubes/chitosan hydrogel film

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ABSTRACT

This research aimed to investigate the adsorption properties and mechanisms of a chitosan hydrogel film incorporated with a 1% mass fraction of multi-walled carbon nanotubes (MWCNTs) to remove Cd(II) from wastewater contaminated with this metal. The hydrogel film exhibited a maximum adsorption capacity of 100.40 mg/g for Cd(II), reaching equilibrium within 360 min and showing optimal adsorption at pH 6. The hydrogel film could be regenerated for up to six cycles with a mere 6% decrease in the removal rate. Mechanistic investigations revealed that Cd(II) ions occupied active sites within the hydrogel film due to its porous structure. Analytical techniques such as Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy confirmed the formation of CdCO_3 during the adsorption process. The adsorption kinetics followed a pseudo-second-order model, and the adsorption isotherm adhered to the Langmuir model, suggesting that monolayer chemical adsorption was the primary mechanism of Cd(II) uptake by the hydrogel film. Temperature and thermodynamic analyses indicated that the adsorption process was spontaneous, endothermic, and led to an increase in entropy. Overall, the incorporation of MWCNTs into the chitosan hydrogel film proved to be an efficient, recyclable, and environmentally friendly approach for the adsorption of cadmium from wastewater contaminated with this metal.

Keywords: Cd(II); Adsorption; Mechanism; Hydrogel

1. Introduction

Cadmium (Cd) is a pervasive heavy metal element in the environment and is considered one of the most dangerous pollutants [1–3]. Cd^{2+} contamination severely affects plant growth and has become a global environmental concern. Furthermore, Cd^{2+} has been classified by the International Agency for Research on Cancer (IARC) as a known human carcinogen (Class 1). Direct exposure or ingestion of Cd^{2+} poses a serious risk to human physical and mental health, leading to mutations, genetic damage, central nervous system impairment, and increased cancer risk. Cd^{2+} pollution not only contaminates water resources but also poses a severe threat to human health, animal life, and vegetation.

Therefore, the urgent treatment of Cd^{2+} -contaminated wastewater requires immediate attention [4–6].

Various methods are currently employed for treating Cd^{2+} polluted water, including adsorption, precipitation, biological treatment, ion exchange, and membrane separation [7–10]. Among these methods, adsorption is particularly favored due to its operational simplicity and wide applicability. The fundamental principle of adsorption is to transfer the ions or atoms of pollutants into the adsorbent, thereby achieving wastewater treatment objectives. Based on different mechanisms, adsorption can be categorized as physical or chemical adsorption. Physical adsorption relies on van der Waals forces between the adsorbent and pollutants, which are generally reversible. In contrast, chemical adsorption

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involves strong chemical bonding between the adsorbent and pollutants, leading to generally irreversible purification effects [11,12]. Researchers have developed various adsorbents for Cd^{2+} removal from wastewater. For instance, Lin et al. [13] developed a chitosan/calcium alginate/bentonite composite physical hydrogel, which simplifies the operation process compared to previous methods. Huang et al. [14] utilized industrial solid waste fly ash mixed with NaOH and $\text{Cd}(\text{OH})_2$, then calcined it at 250°C to obtain modified fly ash with a maximum adsorption capacity of 55.77 mg/g for Cd^{2+} . Tan et al. [15] prepared iron nitrate and potassium permanganate modified biochar, demonstrating a maximum adsorption capacity of 120.77 mg/g for $\text{Cd}(\text{II})$ at 298 K . Additionally, BC-FM maintained a 50% Cd^{2+} removal rate even after being repeatedly used three times. Zhang et al. [16] produced biochar from rapeseed straw powder as the raw material and studied its adsorption capacity for $\text{Cd}(\text{II})$, with the maximum adsorption capacity being 73.3 mg/g .

Effective adsorption relies on the careful selection of adsorbent materials. Recently, three-dimensional porous network structures have gained attention due to their high specific surface area, low density, and renewable nature [17]. Therefore, the development of more efficient and reusable adsorbents in this direction holds significant implications for environmental engineering in pollutant removal [18–20].

Chitosan (CS) is a promising material derived from chitin through deacetylation treatment, and it shows potential for adsorbing water and soil pollutants. The presence of hydrophilic functional groups ($-\text{OH}$, $-\text{NH}_2$, and $-\text{NHCOCH}_3$) in chitosan facilitates the formation of hydrogen bonds with heavy metals and dye pollutants, enabling their chelation [21]. Cross-linking chitosan to form chitosan hydrogel (CH) enhances its mechanical strength and acid stability, while also increasing its specific surface area and porosity, enabling it to absorb water without dissolving. Chitosan hydrogel is an economical and highly adsorptive material for heavy metal ions [22–25]. Multi-walled carbon nanotubes (MWCNTs) possess exceptional adsorption, mechanical, electrical, and thermal properties due to their unique structure, making them excellent candidates for composite materials [26]. In composite materials, MWCNTs provide additional active sites and a larger surface area, making them promising adsorbents. MWCNTs-modified chitosan hydrogel has demonstrated effective pollutant removal from aqueous solutions [27–29].

In this study, we developed a composite film of multi-walled carbon nanotubes and chitosan hydrogel (MWCNTs/CH) for the removal of Cd^{2+} from polluted wastewater. The synthesis involved copolymerizing chitosan with polyvinyl alcohol using the crosslinking agent glutaraldehyde, resulting in an MWCNTs/CH composite film with a loose and porous mesh structure and altered crystallization state. The maximum adsorption capacity of the MWCNTs/CH film was determined to be 100.40 mg/g , indicating a significant adsorption capability. Importantly, the MWCNTs/CH film exhibited excellent recyclability, with only a 6.57% decrease in Cd^{2+} removal efficiency after six cycles of use, demonstrating its robust adsorption capacity. To the best of our knowledge, this is the first report on the utilization of a carbon nanotube/chitosan hydrogel composite film for Cd^{2+} removal, opening up new avenues for future research

on heavy metal ion removal. This innovative approach offers several advantages over conventional techniques, including high adsorption capacity and minimal risk of secondary pollution. Overall, this study contributes to the development of more sustainable and efficient methods for removing heavy metal pollutants from contaminated water and soil systems.

2. Materials and methods

2.1. Materials

The following chemicals were procured from Macklin Chemical Reagent Co., Ltd.: chitosan (>85% deacetylation, AR-grade), glycerin, polyvinyl alcohol (PVA), glutaraldehyde, glacial acetic acid, and CdCl_2 . Furthermore, MWCNTs were obtained from Beijing Boyu Hi-Tech New Materials Co., Ltd.

2.2. Preparation and characterization of the composite adsorbent

To disperse MWCNTs along with chitosan, PVA, and glutaraldehyde (total mass of 1%), 40 mL of deionized water was used in a round-bottom flask at room temperature. Ultrasonic waves were employed for 60 min to achieve the dispersion. Following this, 2.0 g of PVA was added to the flask and allowed to swell for 15 min at 80°C . Then, a sequence of 0.70–0.80 mL glacial acetic acid (AR, 99.5%), 0.56 mL of 2% glutaraldehyde, 32 mL of deionized water, 5 mL of glycerol, and 0.5 g of chitosan were introduced to the flask for cross-linking. The mixture was stirred at 50°C in a water bath for 40 min. Finally, a specific volume of the resulting gel-like liquid was poured onto a flat plate and baked at 90°C for 4 h to obtain the composite adsorbent. Our previous findings indicated that a 1% mass fraction of carbon nanotubes was suitable, as lower fractions resulted in suboptimal adsorption properties, while higher fractions led to non-uniform dispersion. Fig. 1 illustrates the preparation process.

2.3. MWCNTs/CH performance characterization

The morphology and elemental analysis of the sample were examined using a Hitachi S-4800 scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) from Hitachi Corporation, Japan. Surface functional groups were analyzed using a Nicolet-iS50 Fourier-transform infrared spectrometer (FTIR) from Thermo Fisher Scientific Corporation, USA. The crystal structure of the sample was investigated using the XD3 X-ray powder diffractometer (XRD) from Beijing Puxi General Instrument Co., Ltd. Surface elements were analyzed using the K-Alpha™ X-ray photoelectron spectrometer (XPS) from Thermo Fisher Scientific Corporation, USA.

2.4. Adsorption of $\text{Cd}(\text{II})$ in aqueous solution

CdCl_2 was dissolved in deionized water to prepare a solution containing $\text{Cd}(\text{II})$. A 50 mL portion of the $\text{Cd}(\text{II})$ solution with a specific concentration was taken for oscillating adsorption. The resulting supernatant was collected, and its absorbance was measured using flame atomic absorption spectrometry. To minimize errors, all experiments were

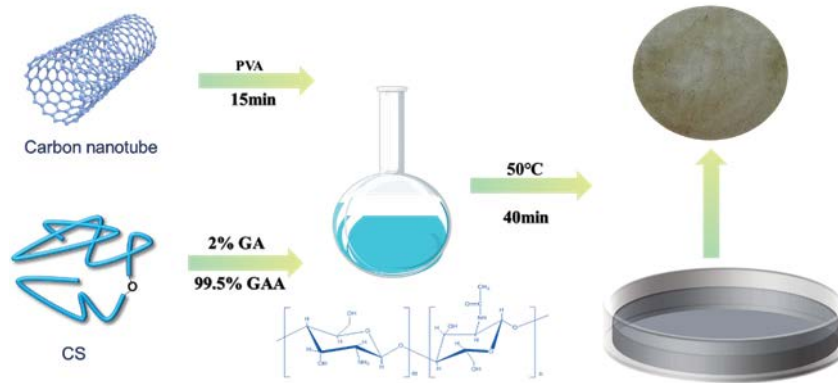


Fig. 1. Flowchart for preparation of the MWCNTs/CH.

performed in triplicate. Initially, a standard curve was constructed using Cd(II) solutions with varying concentrations ($y = 0.04043x + 0.01819$, $R^2 = 0.99831$, where x represents the concentration of the Cd(II) solution and y denotes the absorbance value). Subsequently, the removal rate and adsorption capacity were determined using the following equations:

$$q_e = (C_0 - C_e) \times \frac{V}{M} \quad (1)$$

$$R = 1 - \left(\frac{C_0}{C_e} \right) \times 100\% \quad (2)$$

where C_0 and C_e are the Cd(II) concentrations before and after adsorption (mg/L), V is the adsorbate volume (mL), M is the adsorbent mass (g), and q_e is the equilibrium adsorption capacity of the adsorbent (mg/g). The effects of varying the amount of MWCNTs/CH, initial concentration of the solution, adsorption time, temperature, and pH were considered.

2.5. Cyclic adsorption

To assess the adsorption capacity following each cycle, the composite adsorbents, once they had taken up pollutants, were exposed to a 50 mL NaOH solution (0.1 mol/L) within a conical flask and then positioned on a temperature-controlled shaker. The adsorbent was subsequently rinsed with the remaining NaOH solution at a rate of 100 RPM and a temperature of 25°C over a 2-h period. Any excess water on its surface was eliminated, and the initial desorption was documented. This procedure was carried out six times to determine the reusability and durability of the composite adsorbent.

2.6. Mechanism of adsorption

2.6.1. Equilibrium adsorption

Solutions of CdCl₂ were formulated at concentrations of 2, 4, 6, 8, 10, 15, and 20 mg/L. The adsorption process was conducted at a temperature of 298 K and lasted for 24 h. The adsorption capacity at 298 K was characterized using the Langmuir, Freundlich, and Temkin adsorption isotherms.

Langmuir linear equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b} \cdot q_m \quad (3)$$

Freundlich linear equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n} \right) \ln C_e \quad (4)$$

Temkin linear equation:

$$q_e = A + B \ln C_e \quad (5)$$

This model characterizes the chemical adsorption of monolayers. In this context, C_e denotes the equilibrium concentration of Cd(II) (mg/L), q_e symbolizes the nearing equilibrium adsorption capacity of the adsorbent (mg/g), and q_m represents the potential maximal adsorption capacity (mg/g). Furthermore, b stands for the Langmuir adsorption constant, while K_f and n are Freundlich constants, and A and B serve as constants.

2.6.2. Adsorption kinetics

The adsorption capacity was evaluated at various time intervals at a temperature of 298 K. Three equations were employed to characterize the kinetics of adsorption: the pseudo-first-order equation, the pseudo-second-order equation, and the equation for internal diffusion.

Pseudo-first-order adsorption kinetics:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

Pseudo-second-order adsorption kinetics:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (7)$$

Internal diffusion equation of particles:

$$q_t = k_p t^{1/2} + C \quad (8)$$

where q_t is the adsorption capacity of the adsorbent at time t (mg/g), q_e is the adsorption capacity as adsorption

equilibrium is approached (mg/g), C is a parameter for the internal diffusion equation (mg/g), and k_1 , k_2 and k_p are rate constants.

2.6.3. Adsorption thermodynamics

To evaluate the thermodynamic properties of the hydrogel for adsorbing pollutants, the ΔH , ΔS and ΔG were calculated using the following formulas.

$$K_t = \frac{q_e}{C_e} \quad (9)$$

$$\Delta G = -RT \ln K_t \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

where C_e is the equilibrium adsorption concentration of the Cd(II) (mg/L), q_e is the adsorption capacity of the adsorbent approaching equilibrium (mg/g), ΔG is the free enthalpy (kJ/mol), ΔH is the adsorption enthalpy change (kJ/mol), ΔS is adsorption entropy (J/mol·K).

3. Results and discussion

3.1. Study on Cd(II) adsorption characteristics in aqueous solution

3.1.1. Effect of adsorbent mass on adsorption performance

Fig. 2a illustrates the influence of adsorbent mass on the adsorption performance of MWNTs (1%wt.)/CH for Cd(II). Comparative analysis with previously studied CH adsorption performance reveals a significant enhancement in the adsorption capacity of the hydrogel upon the addition of MWCNTs. At an adsorbent mass of 20 mg, the adsorption capacity and removal rate of MWNTs (1%wt.)/CH were determined to be 85.76 mg/g and 34.30%, respectively. As the mass of the hydrogel increased, the adsorption amount gradually decreased while the removal rate increased until reaching equilibrium. With an adsorbent mass of 100 mg, the adsorption capacity and removal efficiency of MWNTs (1%wt.)/CH were 35.93 mg/g and 71.85%, respectively, reflecting an increase of 16.54% and 10.18% compared to previous values. Further increase in the adsorbent mass slightly improved the removal rate of the hydrogels but marginally decreased the adsorption capacity. The incorporation of MWNTs substantially enhanced the Cd(II) adsorption performance of the chitosan hydrogel due to their extensive specific surface area, which provides more active sites. Furthermore, the results demonstrate that the availability of adsorption sites and removal efficiency increased with higher adsorbent dosage. However, a lower amount of adsorbent exhibited a higher utilization rate in terms of adsorption capacity, while an increase in the amount led to underutilization of adsorption sites, resulting in reduced adsorption capacity per gram of adsorbent. Based on the adsorption capacity and removal rate, 100 mg of MWNTs (1%wt.)/CH hydrogel was selected as the adsorbent for the subsequent experiments.

3.1.2. Effect of initial concentration of Cd(II) on adsorption performance

Fig. 2b presents the influence of the initial concentration of Cd(II) on the adsorption capacity and removal rate. The results indicate that as the concentration of Cd(II) increases, the adsorption capacity also increases while the removal rate decreases. Specifically, as the initial concentration of Cd(II) rises from 50 to 500 mg/L, the adsorption capacity increases from 20.71 to 100.40 mg/g, whereas the removal rate decreases from 82.86% to 40.16%. The number of adsorption sites for Cd(II) on the hydrogels remains constant. The initial concentration of Cd(II) in the solution exhibits a positive correlation with the adsorption capacity of the adsorbent for Cd(II). Once the adsorption sites reach saturation, the impact on the adsorption capacity of Cd(II) becomes minimal. If the concentration of Cd(II) continues to rise, the removal rate gradually decreases.

3.1.3. Effect of adsorption time on adsorption performance

The impact of adsorption time on the adsorption capacity of Cd(II) by the hydrogel is depicted in Fig. 2c. As observed in the figure, the adsorption amount increases with longer adsorption time. The adsorption capacity and removal efficiency of MWNTs (1%wt.)/CH for cadmium were evaluated for solutions with initial concentrations of 10, 20, and 50 mg/L after 1,440 min. For the 10 mg/L solution, MWNTs (1%wt.)/CH exhibited an adsorption capacity of 4.87 mg/g and a removal efficiency of 97.36%. Similarly, for the 20 mg/L solution, the adsorption capacity and removal efficiency were 11.74 mg/g and 93.9%, respectively. In contrast, for the 50 mg/L solution, the hydrogel demonstrated a cadmium adsorption capacity of 20.80 mg/g and a removal rate of 83.02%. The adsorption rate was found to be highest within the first 120 min for all three concentrations. Subsequently, the adsorption rate gradually decreased until reaching 360 min.

3.1.4. Effect of pH on adsorption performance

Fig. 2d presents the results of MWNTs (1%wt.)/CH adsorption at different pH levels. The findings indicate that the absorption of Cd(II) increases with an elevation in pH within the range of 2–6. At pH levels below 4, the absorption capacity is low due to the high concentration of H^+ ions present in the solution under strong acid conditions. These H^+ ions compete with Cd(II) for binding sites, resulting in a reduced capacity for Cd(II) absorption. Additionally, protonation by amino groups leads to the formation of NH_3^+ groups, which generate electrostatic repulsion with Cd(II), thereby reducing available absorption sites and hindering absorption. As the pH increases, H^+ and H_3O^+ ions dissociate from active groups, releasing active sites, and the adsorbent undergoes deprotonation, leading to an increase in both the removal rate and absorption capacity. The optimal pH range for Cd(II) adsorption by the hydrogel is between 6 and 7, where the maximum removal rate (approximately 83.79%) and absorption capacity (around 20.95 mg/g) are observed. These values remain relatively constant within the pH range of approximately 6 to 7. A pH greater than

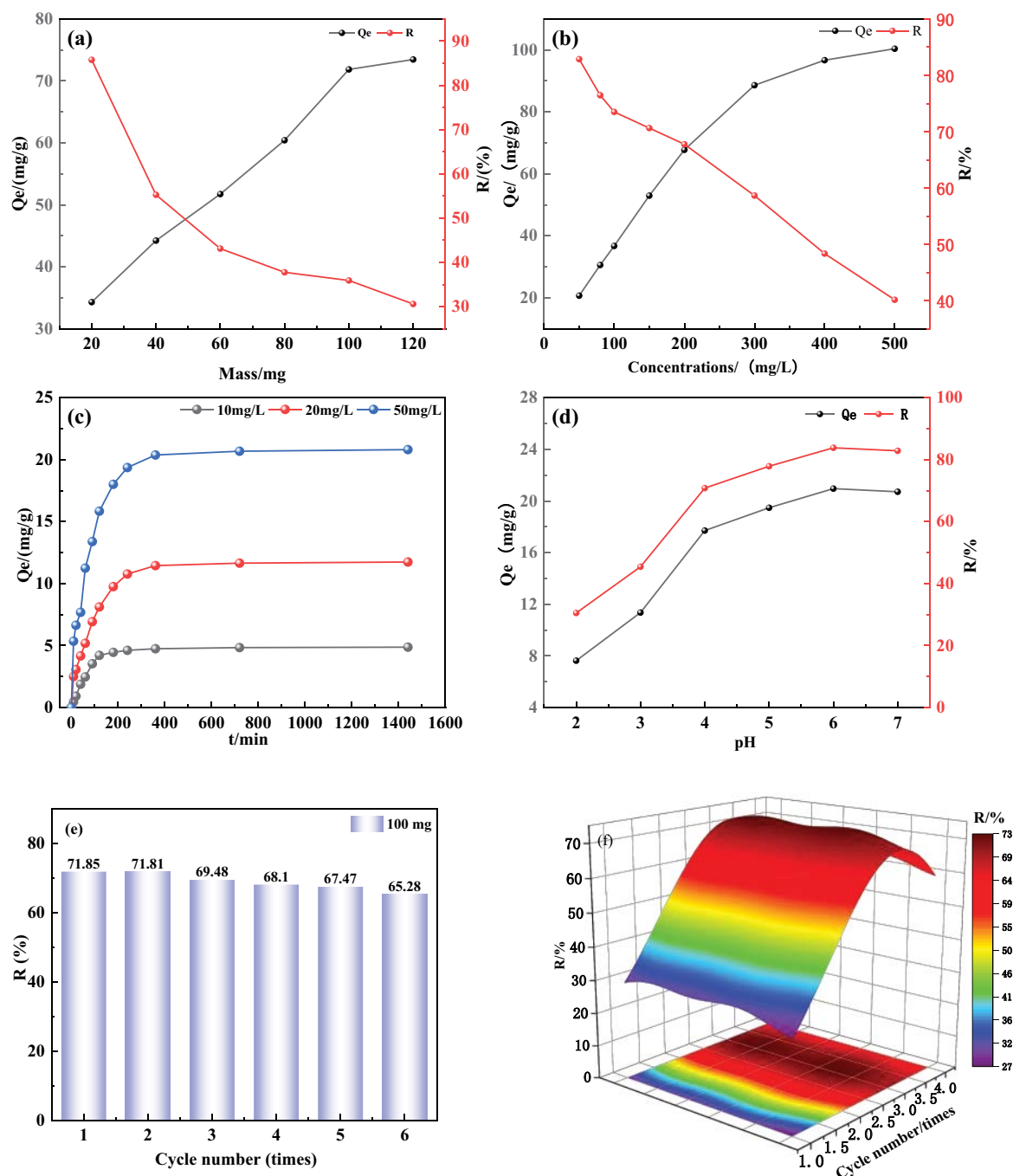


Fig. 2. Effect of adsorbent dosage (a), initial concentration (b), time (c), pH (d) and regenerated times (e,f) on adsorption properties of Cd(II).

7 results in the formation of $\text{Cd}(\text{OH})_2$ compounds, indicating that the optimal pH for Cd(II) adsorption using the hydrogel is between 6 and 7.

3.1.5. Cyclic adsorption

Fig. 2e and f depict the cyclic removal rates of MWNTs (1%wt.)/CH in response to Cd(II) after regeneration. The concentration of the Cd(II) solution was approximately 100 mg/L, while the amounts of MWNTs (1%wt.)/CH varied

at 20, 60, 100, and 150 mg. After three cycles of hydrogel regeneration, the removal rates of Cd(II) slightly decreased from their initial values of 34.30%, 51.74%, 71.85%, and 73.45% to 31.97%, 50.36%, 69.48%, and 71.94%, respectively. The decrease observed was minimal, ranging from 1.38% to 2.37%. Following six cycles of regeneration, the removal rates remained stable at 25.82%, 44.22%, 65.28%, and 67.38%, respectively. In general, the regenerated hydrogel exhibited a decreasing trend in Cd(II) removal rates with each cycle. This decline can be attributed to the strong adsorption

of pollutants during each elution cycle with the NaOH solution, leading to incomplete elution. Nevertheless, the hydrogel maintained its overall morphology and mechanical strength, and it retained a considerable removal rate of Cd(II) even after several cycles.

3.2. Study on the adsorption mechanism of Cd(II) in aqueous solution

3.2.1. Fourier-transform infrared spectroscopy

Fig. 3a presents the FTIR spectra of the MWCNTs/CH film before and after Cd(II) adsorption. The peak observed at the wave number of $1,654\text{ cm}^{-1}$ corresponds to the Schiff base absorption peak of the C=N structure. This peak confirms the cross-linking between chitosan and glutaraldehyde through the reaction between the amino group on the CS chain and the aldehyde group of glutaraldehyde. The absorption peak at $1,416\text{ cm}^{-1}$ represents the deformation vibration of $-\text{CH}_2$, while the peak at 927 cm^{-1} represents the vibration of $-\text{NH}_2$. The addition of MWNTs broadened the band at $3,238\text{ cm}^{-1}$ due to the presence of similar clusters in both CS and MWNTs. The FTIR results suggest that the binding of CS to MWNTs primarily occurred through physical interactions. The stretching vibration of O–H appeared as a peak near $3,287\text{ cm}^{-1}$, while the stretching vibration peaks of C=O in the carboxyl group and CO in CO_3^{2-} appeared at $1,569$ and $1,328\text{ cm}^{-1}$, respectively. After Cd(II) adsorption, the peak at $1,569\text{ cm}^{-1}$ disappeared, indicating the involvement of the carboxyl group on the BC surface in the process of Cd(II) adsorption. These findings demonstrate a significant change in the surface functional groups, mainly $-\text{COOH}$, after Cd(II) adsorption, resulting from the complexation of Cd(II) with the functional groups.

3.2.2. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Fig. 4 displays the SEM images of MWCNTs/CH before (a) and after (b) Cd(II) adsorption. The MWCNTs/CH matrix is characterized by a loose and porous network structure with numerous protrusions and grooves, which contribute to a high specific surface area and enhance its adsorption capacity for pollutants. Importantly, the hydrogel demonstrates excellent stability during the adsorption process, showing no visible particle detachment upon soaking or pulling. The observed filling of surface pores on the hydrogel provides strong evidence for Cd(II) adsorption. This finding is further supported by the EDS spectrum presented in Fig. 3b, which confirms the binding of Cd(II) onto the surface of MWCNTs/CH through adsorption.

3.2.3. X-ray diffraction

Fig. 4c illustrates the XRD patterns of MWNTs/CH films before and after adsorption. The XRD pattern of MWNTs (1%wt.)/CH before adsorption exhibits low crystallinity, characterized by a strong diffraction peak at 2θ of 19.7° , corresponding to the (040) crystal plane of CH. The presence of a weak crystallization peak at $2\theta = 40.4^\circ$ indicates the formation of a small microcrystalline network structure through a chemical cross-linking reaction between chitosan and polyvinyl alcohol. Following adsorption, a new diffraction peak at $2\theta = 14.2^\circ$ appears in the XRD pattern, suggesting the exchange of Cd(II) ions with cations on the material's surface, followed by their capture by minerals or lattices present on the composite material's surface. This transformation results in the conversion of free Cd(II) into an inorganic form. Furthermore, the sharp peak observed in the XRD

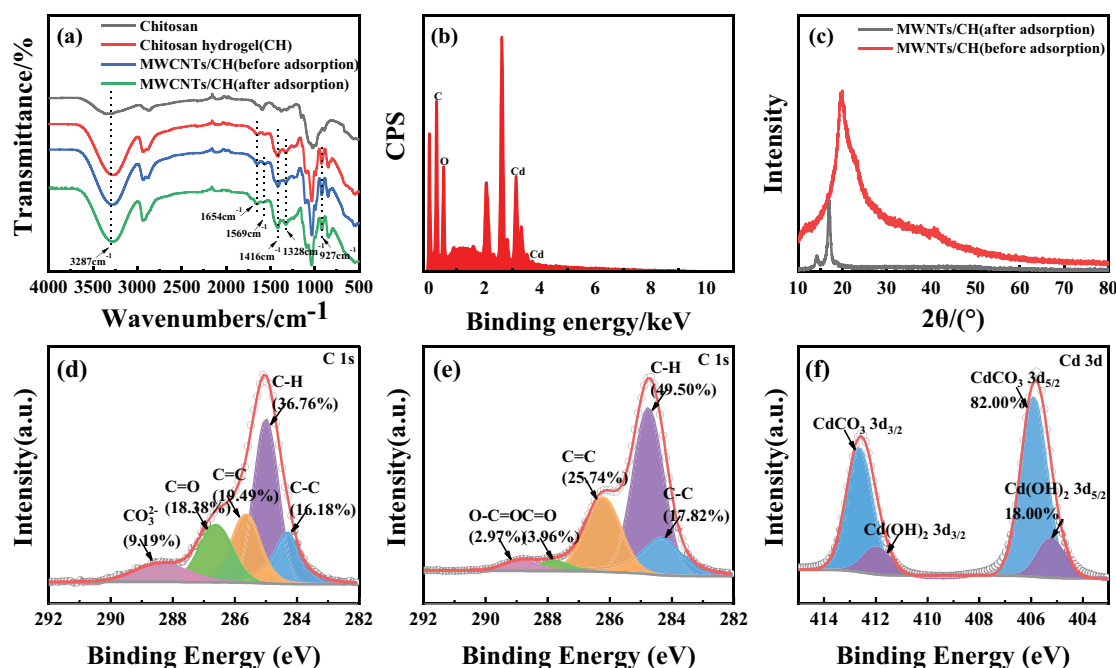


Fig. 3. Fourier-transform infrared spectroscopy (a), energy-dispersive X-ray spectroscopy (b), X-ray diffraction (c) and X-ray photoelectron spectroscopy (d–f) of MWNTs/CH films before and after adsorption.

pattern after adsorption indicates an increase in the lattice constant, indicating that the doped heteroatom cadmium is larger than the original main atom radius. These results demonstrate that the MWCNTs/CH composite material effectively adsorbs Cd(II), and the hydroxyl group forms a complex with Cd(II), as confirmed by the FTIR results. However, due to its low concentration, the XRD pattern does not reveal apparent evidence of cadmium carbonate formation.

3.2.4. X-ray photoelectron spectroscopy

The XPS characterization results before and after Cd(II) adsorption are presented in Fig. 4d–f. Before adsorption, the C1s peak consisted of five distinct components with binding energies of 284.32, 285.00, 285.60, 286.61, and 288.37 eV, corresponding to C–C, C–H, C=C, C=O, and CO_3^{2-} groups, respectively. Following the adsorption of cadmium, the area of the CO_3^{2-} peak decreased to 2.97%, while the area of the C=O peak decreased from 18.38% to 3.96%. These changes suggest the formation of cadmium carboxyl complexes and CdCO_3 -based cadmium precipitation during the adsorption process. These findings align with the results obtained from FTIR and XRD analyses. FTIR analysis showed that there are –OH, C–O, C–H, N–H

functional groups in MWCNTs/CH and these mentioned functional groups can interact with Cd^{2+} in the water media and remove it through complexation and cation- π interaction mechanisms [30]. In addition, the cation exchange and chemical precipitation were effective in removing Cd^{2+} and proved by XRD and XPS [31] (Fig. 5).

3.2.5. Adsorption kinetics

The fitting analysis results, along with the adsorption kinetic parameters for the hydrogel's adsorption of Cd(II), are delineated in Table 1 and Fig. 5a–c. As illustrated in Table 1, the adsorption mechanism of the MWCNTs/CH for Cd(II) aligns with the pseudo-second-order kinetics, displaying determination coefficients R^2 exceeding 0.995. The maximal adsorption capacity, derived from the pseudo-second-order kinetics, closely mirrored the actual measured values. This suggests that the adsorption process is predominantly governed by chemical adsorption. Fig. 5a–c depict the fitting models for the adsorption kinetics of Cd(II) by MWCNTs/CH. These discoveries offer pivotal insights for the conceptualization and enhancement of hydrogel-based adsorbents, aiming at the extraction of heavy metal ions from water-based solutions.

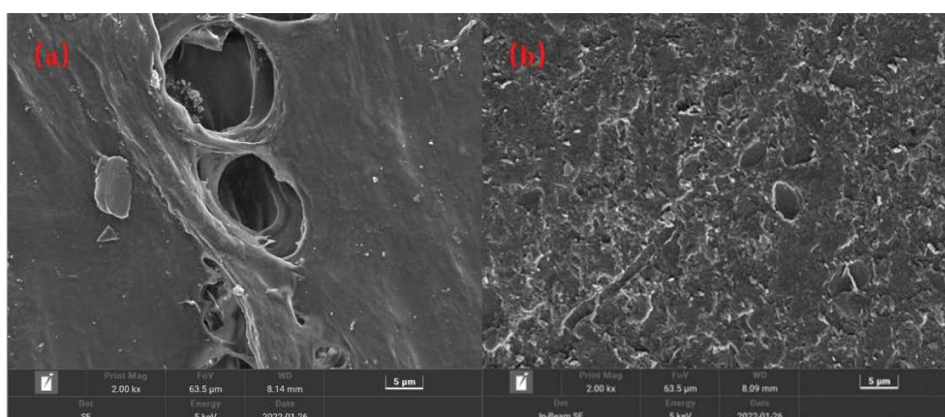


Fig. 4. Scanning electron microscopy of MWCNTs/CH films before (a) and after (b) adsorption.

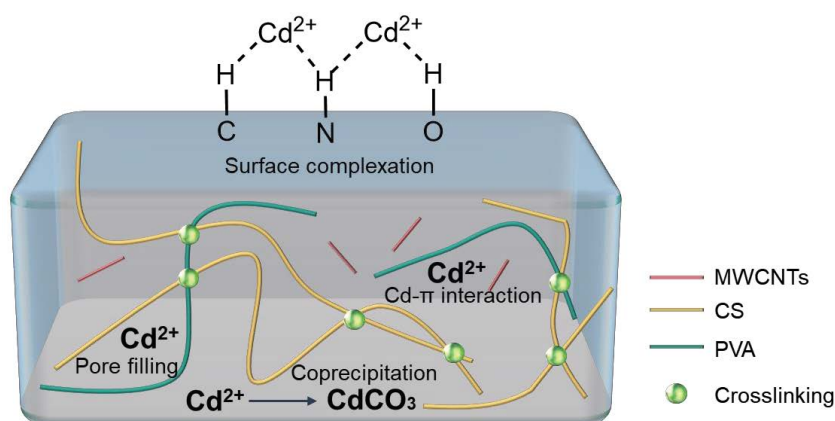


Fig. 5. Mechanisms of Cd^{2+} removal by MWCNTs/CH.

Table 1
Kinetic model parameters for the adsorption of Cd(II) of MWCNTs/CH

Concentration (mg/L)	$Q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
		$Q_{e(\text{cal})}$ (mg/g)	k_1 (min ⁻¹)	R^2	$Q_{e(\text{cal})}$ (mg/g)	k_2 (g/mg·min)	R^2	k_p (mg/g·min ^{1/2})	C	R^2
10	4.868	2.670	0.00688	0.862	5.123	0.00014	0.995	0.11944	1.6767	0.529
20	11.737	8.212	0.00697	0.931	12.323	0.00144	0.998	0.28612	3.7234	0.673
50	20.799	12.998	0.00726	0.932	21.603	0.00107	0.999	0.46517	7.9374	0.637

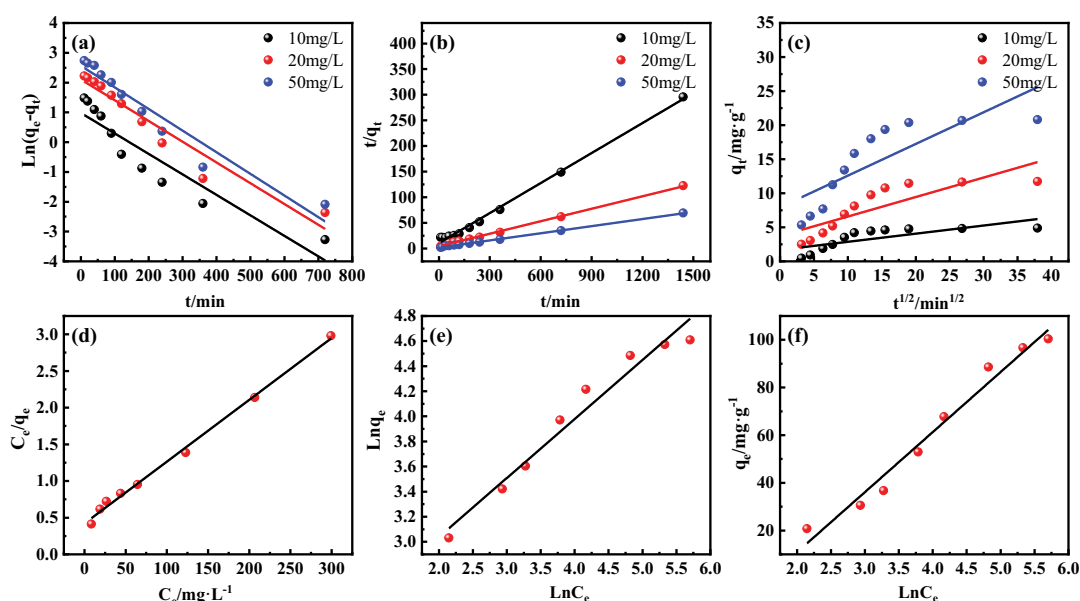


Fig. 6. Fitting model for adsorption kinetics of Cd(II) by hydrogel (a) pseudo-first-order model, (b) pseudo-second-order model, (c) intraparticle diffusion model and isotherm model fitting of Cd(II) adsorption on hydrogel (d) Langmuir, (e) Freundlich and (f) Temkin models.

Table 2
Isothermal model parameters of Cd(II) adsorption by hydrogel

Langmuir model				Freundlich model			Temkin model		
q_m	K_L	R_L	R^2	K_f	$1/n$	R^2	A	B	R^2
118.624	0.0201	0.499	0.995	8.1416	0.470	0.957	-39.4961	25.1966	0.971

3.2.6. Adsorption isotherm

The isothermal model fitting for Cd(II) adsorption onto MWCNTs/CH is depicted in Fig. 6a–c. The R^2 value of the Langmuir model (0.995) was significantly larger than that of the Freundlich model (0.957), indicating that the adsorption of Cd(II) by hydrogel was mainly monolayer chemical adsorption. The maximum adsorption capacity, as determined from the Langmuir model, was 118.62 mg/g, highlighting the hydrogel's impressive adsorptive efficacy for Cd(II). The fitted value of $0 < 1/n = 0.470 < 1$ suggests a robust interaction between the hydrogel and Cd(II). Furthermore, the separation factor of $0 < R_L = 0.499 < 1$ signifies that Cd(II) adsorption is advantageous. The isothermal

model parameters pertaining to Cd(II) adsorption onto the hydrogel are detailed in Table 2.

3.2.7. Adsorption thermodynamics

The influence of temperature on the Cd(II) adsorption mechanism was assessed by examining hydrogel adsorption at 298, 308, and 318 K. The findings revealed that as temperature rose, the efficacy of Cd(II) removal by the hydrogel also enhanced. Specifically, the removal percentages stood at 82.89%, 87.15%, and 89.60% for 298, 308, and 318 K, respectively. As the temperature increased, the thermal motion of Cd(II) also escalated, resulting in augmented interactions

between Cd(II) and the hydrogel, which in turn elevated the Cd(II) removal rate. These observations shed light on tailoring temperature parameters for optimal extraction of heavy metal ions via hydrogel-based adsorbents.

In a related exploration, temperature's role in the Cd(II) adsorption dynamics was probed employing thermodynamic equations. The data underscored that the hydrogel-mediated adsorption of Cd(II) is a spontaneous phenomenon, as evidenced by $\Delta G < 0$. Moreover, the rising absolute magnitude of ΔG indicates diminishing favorability of adsorption at elevated temperatures. The value $\Delta H = 22.73$ kJ/mol, surpassing 20 kJ/mol, denotes that the Cd(II) adsorption encompasses both physical and chemical processes, signifying an endothermic nature. The uptick in temperature facilitated the reaction, aligning with the observed pattern of Cd(II) adsorption enhancement with temperature increments. Concurrently, a ΔS value of 83.73 J/mol·K implies that the adsorption mechanism contributes to an expanded system's entropy, suggesting an entropy-driven shift upon achieving adsorption equilibrium.

4. Conclusion

The data suggest that Cd(II) was more proficiently adsorbed by varying quantities of MWNTs (1%wt.)/CH in comparison to the CH hydrogel alone. When the MWNTs (1%wt.)/CH dose reached 100 mg, the Cd(II) removal efficiency ascended to 71.85%. The most favorable adsorption of Cd(II) manifested at a pH of 6, and the hydrogel's adsorptive quantity intensified over time, stabilizing after 360 min. Moreover, the peak adsorption capability of MWNTs (1%wt.)/CH for Cd(II) was determined to be 100.40 mg/g at the outset concentration.

When adsorbed onto the active sites of the porous MWNTs/CH films, Cd(II) engaged in intricate reactions, culminating in the genesis of inorganic compounds, including CdCO_3 . The adsorption dynamics conformed to the pseudo-second-order kinetic model and the Langmuir isothermal adsorption framework. This suggests that the adsorption of Cd(II) by the hydrogel was chiefly characterized by monolayer chemical adsorption. A comprehensive evaluation of temperature and thermodynamics inferred that the adsorption mechanism of Cd(II) by the hydrogel was spontaneous, displayed endothermic attributes, and resulted in heightened entropy.

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Supporting information

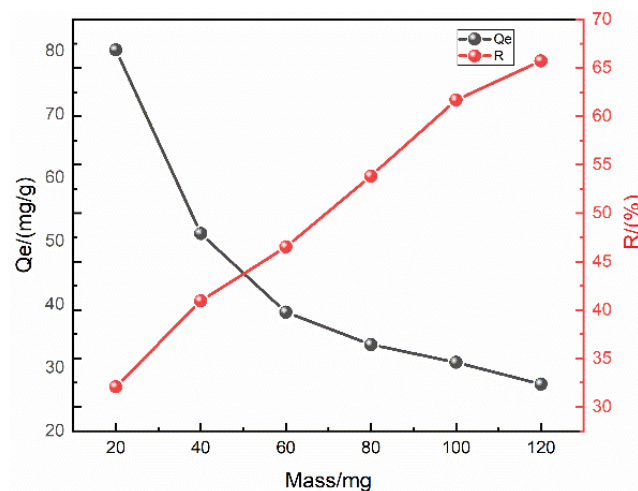


Fig. S1. Effect of adsorbent mass of pure CH.