

Article

Synthesis of Carboxymethylcellulose–Acrylamide–Montmorillonite Composite Hydrogels for Wastewater Purification

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Abstract: The three-dimensional network and ample pore structure of novel hydrogel materials enable outstanding adsorption performance for pollutants such as methylene blue (MB) and Cr⁶⁺ ions in wastewater. In order to develop an environmentally friendly hydrogel with high adsorption performance and low cost, a type of carboxymethyl cellulose (CMC) composite hydrogel was synthesised with montmorillonite (MMT) via chain radical polymerization, which gives it great potential for application in the field of wastewater purification. A series of hydrogel samples were characterised through SEM, FTIR and nitrogen porosimetry analysis, indicating the successful intercalation of MMT nanosheets into the hydrogel crosslinking network. The mass ratio of CMC to MMT, the amounts of adsorbent, the initial concentration of wastes, pH, and the adsorption temperature were investigated and optimised for hydrogel adsorption performance. When the initial concentration of MB is 60 mg/L, pH is 7, the dosage of MB is 0.5 g/L, and the adsorption temperature is 30 °C, the hydrogel sample the highest adsorption capability for MB removal, with an adsorption amount of 112.9 mg/g. When the initial concentration of Cr⁶⁺ is 10 mg/L with a pH of 7, the highest adsorption capacity of the hydrogel for Cr⁶⁺ removal is 1.35 mg/g. The fitting results of the isothermal models, the kinetic models, internal particle diffusion models and the thermodynamics of the experimental data of the adsorbate adsorption process show that the adsorption of MB by hydrogel is a spontaneous segmented process of multi-layer physical and chemical adsorption. Additionally, the adsorption of Cr⁶⁺ ions by hydrogel is a spontaneous segmented process of multi-layer physical adsorption.

Keywords: composite hydrogel; adsorption performance; wastewater purification



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1. Introduction

In recent years, with the rapid growth of the population and the high speed of industrialization, water pollution has gradually evolved into one of the most important environmental problems in society [1]. The main sources of water pollution are heavy metal ions and organic dyes [2,3]. Heavy metal ions, such as Cr⁶⁺, Cd²⁺, Hg²⁺, Pb²⁺, etc., not only seriously pollute the water body, soil, and the atmosphere, but also enter the human body through the food chain and the bio-concentration effect. This inhibits human growth and development, and excessive accumulation can even lead to diseases such as cancer, high blood pressure and kidney failure. As one of the most widely used dyes in the textile industry, methylene blue (MB) not only inhibits the photosynthesis of aquatic organisms, but also seriously disrupts the ecological balance of water bodies. It can also cause dizziness, nausea, respiratory distress, diarrhoea, vomiting, anaemia, and even neurological damage when ingested into the human body [4,5].

Traditional wastewater treatment techniques include chemical oxidation [6,7], biodegradation [8,9], adsorption [10–12], membrane separation [13,14], flocculation [15,16], chemical precipitation [17–19] and ion exchange [20,21]. Among them, adsorption method is considered as one of the most effective methods for the removal of heavy metal ions and organic dyes due to its simplicity of operation, wide range of application, cost-effectiveness and environmental friendliness. In recent years, traditional adsorbents such as artificial resins and activated carbon have been widely used because of their advantages such as low cost. However, they are subject to many limitations due to their low adsorption efficiency, easy clogging and poor regeneration performance [22,23]. These adsorption materials, such as zeolites [24], metal–organic frameworks (MOFs) [25–27], hydrogels [28,29], and aerogels [30–33], have gradually appeared in people’s field of vision.

In 1960, Wichterle and Lím synthesised the first generation of hydrogels [28]. As three-dimensional materials, hydrogels have excellent properties such as large specific surface area, high porosity, and excellent water absorption, which give them great potential for application in the field of wastewater purification [34,35]. There are many kinds of hydrogels, such as chitosan-based hydrogels [36,37], cellulose-based hydrogels [38,39], hyaluronic acid hydrogels [40,41], pectin hydrogels [42], etc. However, it is difficult for hydrogels prepared with a single material to meet application needs. Adding other materials to prepare hydrogels with excellent comprehensive properties has become the mainstream trend at present [43]. Chen et al. [29] synthesised an agar/poly (acrylamide-co-hydroxyethyl acrylate) double-network hydrogel, which had good effect on the removal of Pd^{2+} and Cd^{2+} . Li et al. [44] reported a cationic adsorbent poly (epichlorohydrin)-ethylenediamine hydrogel (PEE-Gel), and the adsorption results showed that its maximum adsorption capacity for anion dye Congo red (CR) could reach 1540 mg/g.

Carboxymethyl cellulose hydrogel has functional groups such as $-\text{COOH}$ and $-\text{OH}$ on its backbone, which have a strong affinity for pollutants. It not only has the advantages of fast adsorption rate, high adsorption rate, and recyclability as an adsorbent, but also has good biodegradability and biocompatibility [45,46]. In addition, the three-dimensional network pore structure of cellulose hydrogel endows it with strong flexibility, permeability, and the ability to absorb and retain water [47]. Godiya et al. [39] prepared a CMC/PAM composite hydrogel using free radical polymerization of CMC and polyacrylamide (PAM), which was efficiently adsorbed through its good monoanionic affinity for Cu^{2+} . Chen et al. [48] used sodium carboxymethyl cellulose, polyacrylic acid, and polyacrylamide as raw materials to prepare the bio-sorbent CMC-PAMA via a simple thermal cross-linking method for the adsorption of MB. It was shown that a large number of intermolecular hydrogen bonds increased the stability of the structure of CMC-PAMA, resulting in good adsorption of the cationic dye MB. However, the poor mechanical properties and single function of cellulose hydrogel greatly limit its practical application.

Montmorillonite (MMT) has great potential for application in wastewater adsorption due to its excellent cation exchange capacity and layered structure. Through techniques such as chemical peeling [49] and mechanical peeling [50], montmorillonite can be stripped into single or multiple nanosheets. Peeled MMT nanosheets (MMTNS) have small size and high dispersion, and they can be composited into the three-dimensional network structure of the hydrogel, which can effectively improve the comprehensive properties of hydrogel, including its water retention, salt resistance, mechanical strength, and thermal stability [51]. Nie et al. [52] prepared (DMPMA-co-AA)/Mt composite hydrogel via in situ intercalation polymerization using N-(3-dimethylaminopropyl) methacryloyl and acrylic acid as monomers and montmorillonite as fillers. The compressive strength of the composite hydrogel reached 54.4 kPa at 99.8% water content. Irani et al. [53] prepared acrylic–starch/montmorillonite hydrogels with good mechanical strength by adding montmorillonite to acrylic–starch through emulsion polymerization. The composite hydrogel has good water absorption up to 800 g/g.

In this work, in order to develop an hydrogel with high adsorption performance that is cost-effective, easy to operate, and environmentally friendly, MMT was introduced

into the sodium carboxymethylcellulose (CMC)–acrylamide (AM) system, and a CMC–AM–MMT composite hydrogel was prepared via chain radical polymerization with *N,N*-methylenebis-acrylamide (MBA) as a crosslinking agent and sodium persulfate as an initiator. The effects of matrix ratio, initiator, crosslinker dosage, adsorbent dosage, shock time, temperature, and pH on the adsorption of Cr^{6+} and methylene blue in hydrogel were also investigated. We also carried out a variety of characterizations of hydrogels under optimal preparation conditions, explored the surface structure and properties of hydrogels, analysed the adsorption kinetics isothermal models, internal particle diffusion models and thermodynamics of hydrogels, and explained the mechanism of hydrogel adsorption of Cr^{6+} and methylene blue.

2. Experimental

2.1. Materials

Chemicals including sodium carboxymethyl cellulose, acrylamide, *N,N'*-methylenebis-acrylamide, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), methylene blue, absolute ethanol, potassium dichromate, phosphoric acid, sulfuric acid, acetone, and diphenyl carbamide were purchased from Aladdin Co., Ltd., Shanghai, China. MMT was purchased from Nacor Corporation (cation exchange capacity: 145 m equiv / 100 g, particle size: 16–22 μm), and had not been otherwise processed before use. Reagents of analytical grade and deionised water were used for the experiments.

2.2. Preparation of CMC–AM Hydrogel

The hydrogel sample was fabricated by following a previously published procedure with necessary modifications [47]. The mass ratio of CMC was varied to investigate the optimized preparation conditions of the hydrogel sample. A certain mass of CMC was accurately weighed and dissolved in deionised water to prepare CMC solutions with different mass proportions. Subsequently, 6 wt% of AM as a monomer, 0.6 wt% of MBA as a crosslinker, and 0.6 wt% of sodium persulfate as an initiator were added to the beaker and stirred. The formed gel was removed after heating at 70 °C for 4 h. The gel was rinsed with water and soaked three times for 8 h each, and finally freeze-dried at −60 °C to obtain the prepared hydrogel samples. According to different CMC contents (1 wt%, 2 wt%, 3 wt%, 4 wt%), the hydrogel samples were labelled CMC₁–AM, CMC₂–AM, CMC₃–AM, and CMC₄–AM, respectively.

2.3. Preparation of CMC–AM–MMT Hydrogel

The preparation process of CMC–AM–MMT hydrogel was based on CMC–AM hydrogel, except for the introduction of MMT materials. A certain mass of CMC was dissolved in deionised water to prepare 3 wt% CMC solution. A certain mass of MMT was added to deionised water, and sonicated for 30 min to prepare MMT solutions with different mass fractions (0, 1 wt%, 2 wt%, 3 wt%, 4 wt%). The MMT solution was then added into the CMC solution, followed by the addition of 6 wt% of AM, 0.6 wt% of MBA and 0.6 wt% of sodium persulfate under mixing. The gel was sealed and removed after constant heating at 70 °C for 4 h. The gel was rinsed with water and soaked three times for 8 h each, and finally freeze-dried at −60 °C. The mass ratio of CMC and MMT was varied to investigate the optimised preparation conditions of the hydrogel sample. According to different CMC: MMT contents (3:1, 3:2, 3:3, 3:4), the hydrogels were labelled CMC–AM–MMT₁, CMC–AM–MMT₂, CMC–AM–MMT₃, and CMC–AM–MMT₄, respectively.

2.4. Characterization

The hydrogel samples were characterised using various techniques, including SEM, FTIR and nitrogen porosimetry analysis. A series of freeze-dried composite gel samples were sliced and glued to the conductive plate with conductive glue, and the surface was sprayed with gold and placed in a scanning electron microscope (ZEISS Merlin, Ottobrunn, Germany) to observe the morphology of the composite gel samples at a scanning voltage

of 5 kV. The freeze-dried hydrogels were ground into powder and added to potassium bromide, after which they were mixed and pressed into sheets, which were then characterised via Fourier infrared spectroscopy (VERTEX 70, Ettlingen, Germany) with a scanning wavenumber ranging from 400 cm^{-1} to 4000 cm^{-1} . An ASAP2460 automated specific surface area and porosity analyser was employed to obtain N_2 isothermal adsorption and desorption results on the prepared CMC hydrogel at $140\text{ }^\circ\text{C}$ for 12 h.

2.5. Adsorption Performance Analysis of Methylene Blue

A certain amount of hydrogel sample was added to 100 mL of methylene blue solution and put into a shaker for 6 h (160 rpm/min). The liquid was filtered through the needle filter (Aqueous phase, $0.22\text{ }\mu\text{m}$), then 1 mL of liquid was taken, and the absorbance of the colorimetric tube sample was measured at 665 nm with a UV-Vis spectrophotometer. The residual concentration of adsorption was calculated using the standard curve, and then the removal efficiency and other parameters were calculated using the equation. The effects of CMC components, oscillation/standing conditions, hydrogel dosage, methylene blue concentration, temperature, and adsorption time on the adsorption efficiency of hydrogel were investigated.

2.6. Adsorption Performance Analysis of Cr^{6+} ions

A certain amount of hydrogel sample was added to 100 mL of chromium-containing wastewater simulated using potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$); this was shaken in a shaker at different temperature for 6 h (160 rpm/min). After passing through a needle filter (aqueous phase, $0.22\text{ }\mu\text{m}$), 1 mL of liquid it was taken and diluted with water by 50 times to set the volume; sulfuric acid, phosphoric acid, and colour-rendering agent (diphenyl carbamide) were added. The absorbance was measured at 540 nm with a UV-Vis spectrophotometer to determine the concentration of Cr^{6+} using the standard curve. The effects of Cr^{6+} components, simulated chromium-containing wastewater concentration, hydrogel dosage, oscillation time, temperature, and pH on the adsorption efficiency of hydrogel were investigated.

2.7. Calculation Analysis

The concentration of the wastewater before adsorption, recorded as C_0 , the concentration after adsorption, recorded as C_t , and the removal rate can be calculated according to Equation (1).

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

C_0 is the initial concentration of the adsorbate (mg/L); C_t is the concentration value of the adsorbed solution at the t moment (mg/L); and η is the removal efficiency of pollutants in water.

Adsorption capacity is calculated using the volume of adsorbent, calculated according to Equation (2).

$$Q = \frac{(C_0 - C_t)V}{m} \quad (2)$$

C_0 and C_t are the same as above Equation (1); m is the mass of the hydrogel (g); V is the adsorbate solution volume (mL); and Q is the mass (mg/g) per gram of adsorbent adsorbed.

The kinetics of dye adsorption are used to simulate the relationship between time and adsorption amount during the adsorption process using suitable kinetic models such as pseudo-primary and secondary adsorption. Pseudo-primary and secondary-order equations are used as shown in Equations (3) and (4).

① Pseudo-first-order kinetic model:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

Q_t is the adsorption capacity (mg/g) representing the adsorption of adsorbent at time t ; Q_e represents the equilibrium adsorption capacity (mg/g); t is the adsorption time (min); and k_1 stands for the kinetic model constant (min^{-1}).

② Pseudo-second-order kinetic model:

$$Q_t = \frac{Q_e^2 \times k_2 t}{1 + Q_e \times k_2 t} \quad (4)$$

Q_t , Q_e , t are the same as in the above Equation (3); k_2 represents kinetic adsorption rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

The internal particle diffusion is described using the Weber and Morris (W&M) model [54]:

$$Q_t = k_{W\&M} t^{1/2} \quad (5)$$

Q_t , t are the same as in the above Equation (3); $k_{W\&M}$ is estimated by plotting Q_t vs. Q_e .

Briefly, 50 mg of hydrogel was added to 200 mL MB and Cr^{6+} solution at a concentration of 10–100 mg/L to investigate the isothermal adsorption of MB and Cr^{6+} . The data were fitted using the Langmuir (6) and Freundlich (7) models.

① Langmuir model:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

Q_m (mg/g) is the maximum adsorption capacity of hydrogel; C_e (mg/L) and Q_e (mg/g) are the equilibrium concentrations and the equilibrium adsorption capacity of dye or metal ion in aqueous solution, respectively; and K_L (L/mg) are the Langmuir isotherm constants.

② Freundlich model:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Q_t , Q_e , t are the same as in the above Formula (6); the parameters K_f ($\text{mg}^{(1-1/n)} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$) and n are the adsorption capacity coefficient and adsorption intensity coefficients, respectively.

The values of thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using the following equations [55,56]:

$$\Delta G^\circ = -RT \ln K_o \quad (8)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

K_o is the Langmuir constant ($\text{L} \cdot \text{mol}^{-1}$) and equal to Q_e/C_e , R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is the reaction temperature (K). The values of ΔH° and ΔS° are obtained from the slope and intercept of the line plotted using $\ln K_o$ versus $1/T$, respectively.

The bulk density of hydrogels (ρ_a) is their weight-to-volume ratio. The porosity of hydrogels is calculated following Equation (10):

$$\varphi = \left(1 - \frac{\rho_a}{\rho_b}\right) \times 100\% \quad (10)$$

where ρ_b ($\text{g} \cdot \text{cm}^{-3}$) is the average skeletal density of the hydrogel.

3. Results and Discussion

3.1. Characterization of the CMC Hydrogel

As shown in Figure 1, the hydrogel sample was synthesised via chain radical polymerization with CMC and AM. In the presence of the $\text{Na}_2\text{S}_2\text{O}_8$ initiator, the CMC portion is performed as the main skeleton of the hydrogel, and the sulfate anion attacks the hydrogen atoms on the hydroxyl group of the CMC backbone to produce a redox system, thereby initiating the grafting of AM on the CMC. In the presence of a crosslinker (MBA), the

AM chain is lengthened and crosslinked. Finally, a complete CMC gel network system is formed. MMT can play a role in supporting the gel skeleton structure, as well as providing the active adsorption site for containment removal.

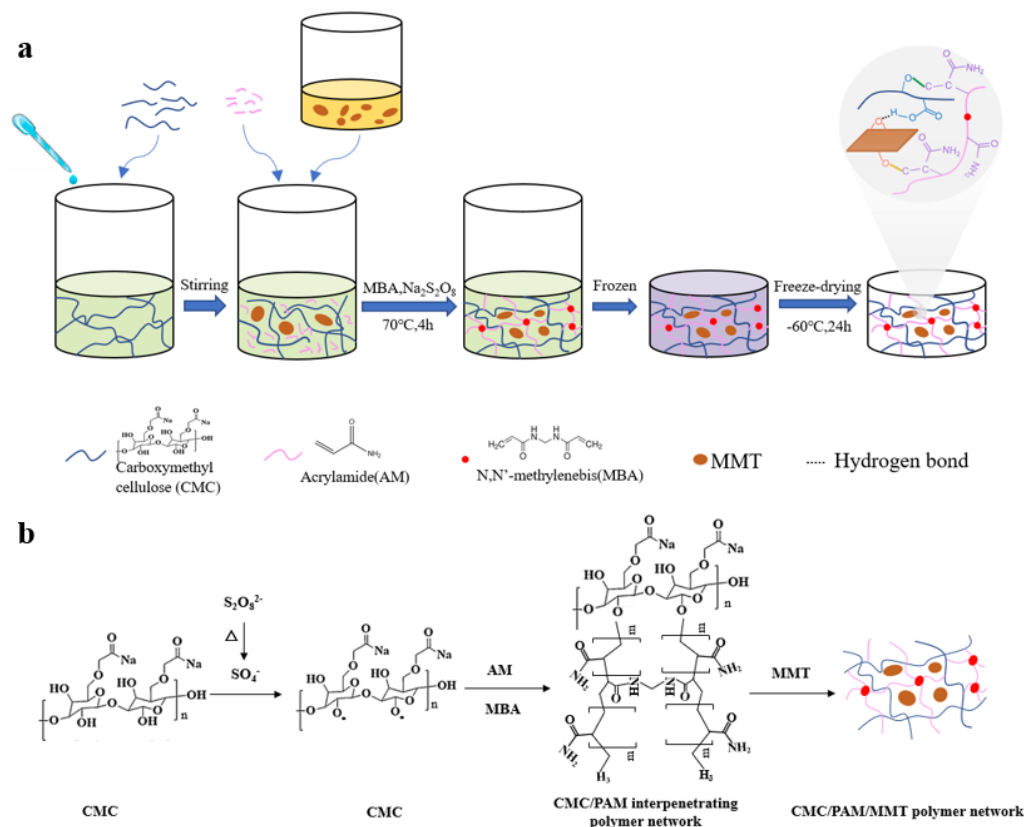


Figure 1. (a) Preparation process of CMC-AM-MMT hydrogel; (b) CMC-AM-MMT hydrogel interpenetrating polymer network mechanism.

The infrared spectra of the composite hydrogel are shown in Figure 2. The characteristic peaks at 3335 cm^{-1} , 2920 cm^{-1} and 1315 cm^{-1} represent the vibration of the -OH bond, the stretching vibration of the C-H bond, and the bending vibration of the CMC bond, respectively [57,58]. The ether bond of the CMC ring appeared at 1199 cm^{-1} . It should be noted that the composite hydrogels show relatively obvious new characteristic absorption peaks at 3178 cm^{-1} , 1610 cm^{-1} and 1428 cm^{-1} , assigned to the characteristic peaks of -NH , C=O and C-N in the -CO-NH_2 groups in polyacrylamide, respectively [47]. The intensity of the peak at 1075 cm^{-1} of the CMC is significantly weakened due to its graft copolymerization with AM. The peak at 1648 cm^{-1} is attributed to carboxamide group vibration, and the displacement of the peak from 1673 cm^{-1} to 1648 cm^{-1} in the composite hydrogel confirms the grafting of AM onto the CMC backbone [59], suggesting a successful polymerization of PAM in the network of CMC gel. The MMT shows an absorption peak at 3633 cm^{-1} , which belongs to the hydroxyl group vibration from the Al-OH structure. However, this peak disappeared in the composite hydrogel, indicating that AM was grafted onto MMT. The bands at 1032 cm^{-1} and 452 cm^{-1} are assigned to the Si-O-Si stretching and bending vibrations from MMT [39].

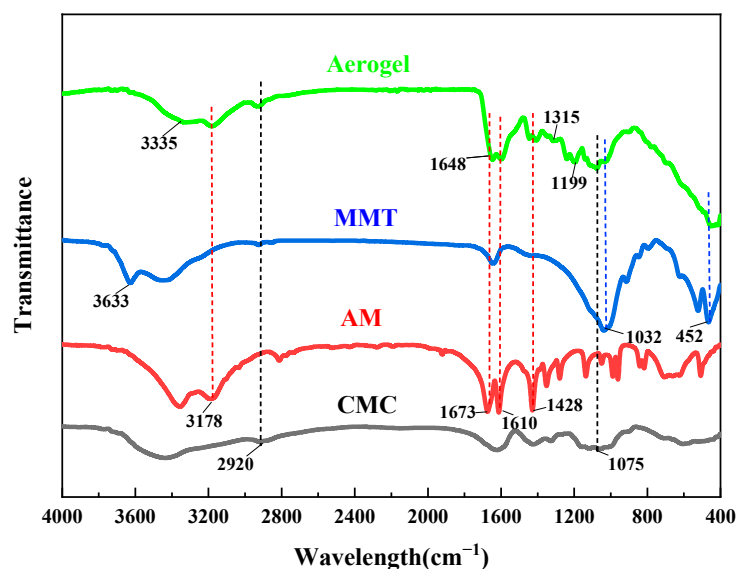


Figure 2. FTIR spectra of the CMC-AM-MMT hydrogel, MMT, AM, and CMC samples.

Table 1 shows the shrinkage, density, porosity and BET of hydrogels with different MMT doping amounts. As can be seen from Table 1, the shrinkage of hydrogels decreases with the increase in MMT doping, along with a high porosity value of greater than 90%. In the hydrogel without MMT nanosheets, the shrinkage rate and density are high due to the lack of MMT support, indicating that the hydrogel undergoes greater pore structure collapse during the drying process. For the samples prepared with more MMT-doped amounts, the shrinkage rate decreased, and the gel skeleton structure was preserved.

Table 1. Shrinkage, density, and BET of CMC-AM-MMT hydrogels with different MMT-doped amounts.

CMC:MMT	Shrinkage	Density (ρ) g/cm ³	BET m ² /g	Porosity (ϕ)
3:0	26.32%	0.0812	1.21	93.55%
3:1	17.54%	0.0785	1.26	93.53%
3:2	12.42%	0.0846	2.54	93.25%
3:3	8.33%	0.0881	3.08	93.17%
3:4	7.95%	0.0896	2.44	92.95%

The micro-morphology of the as-synthesised hydrogels was observed via SEM microscopy. As shown in Figure 3a, the CMC₃-AM sample was successfully prepared to form a three-dimensional porous structure with a neat surface, and the pore size was on the micrometre scale. Figure 3b–e show microscopy images of the hydrogel samples prepared with the incorporation of MMT nanosheets. As can be seen from the figure, the uniformly sized MMT sheets are evenly distributed over the hydrogel surface, so that the CMC surface contains very rich groups, such as -OH, -NH₂, -COOH, etc., contributing to an improvement in the adsorption capability of the CMC-AM-MMT hydrogel. As MMT continues to increase, CMC-AM-MMT hydrogel in Figure 3e agglomerates. Therefore, it can be seen from the SEM images that the CMC-AM-MMT₃ sample possesses high MMT loading, while avoiding agglomeration.

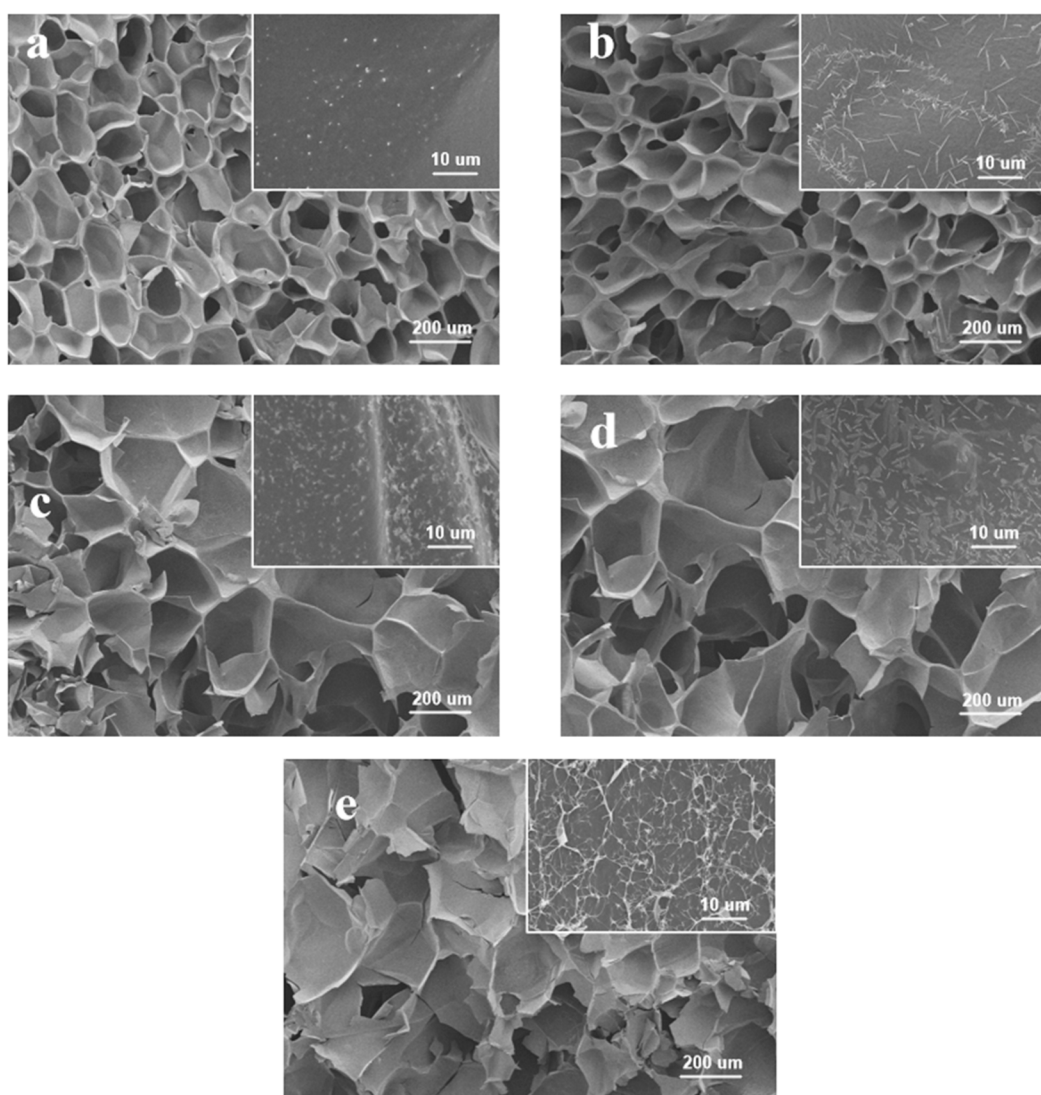


Figure 3. SEM images of (a) CMC₃-AM, (b) CMC-AM-MMT₁, (c) CMC-AM-MMT₂, (d) CMC-AM-MMT₃, and (e) CMC-AM-MMT₄ hydrogel.

3.2. Methylene Blue Removal Performance

3.2.1. Initial CMC and MMT Content

Figure 4a,b shows the MB adsorption capacity and removal rate of the CMC-AM-MMT hydrogels prepared with different CMC and MMT amounts. It can be seen from the figure that the adsorption capacity of the hydrogel without MMT incorporation is proportional to the amount of CMC. This is because that with the increase in CMC content, the number of carboxyl groups in the sample increases, and thus the complexation ability with MB is enhanced. When the amount of CMC further increases, although the number of carboxyl groups increases, the gel volume is limited, and its internal pores are compressed, which affects the adsorption amount and removal rate of dyes by the gel. For the samples prepared with the MMT, the adsorption capacity of hydrogel is also positively correlated with the amounts of MMT. This is because MMT acts as the skeleton structure of the hydrogel, which increases the porosity of the gel and thus improves the adsorption capacity of the gel. In addition, MMT is introduced into the hydrogel system. The cation exchange capacity of CMC-AM-MMT hydrogel is increased due to the increase in the Na⁺ ratio. More MB carrying a positive charge is exchanged or adsorbed to the active site of the CMC-AM-MMT hydrogel. When the amount of MMT reaches a certain extent, MMT is not

evenly distributed on the hydrogel surface, resulting in agglomeration, which reduces the homogeneity of the hydrogel structure. The pores of the gel cannot continue to expand, and the adsorption capacity of MB cannot be enhanced. Therefore, when the amount of CMC is 3 g and the mass ratio of CMC to MMT is 1, the adsorption performance of CMC-AM-MMT hydrogel is optimal. Further adsorption experiments were carried out with CMC₃-AM and CMC-AM-MMT₃ hydrogel.

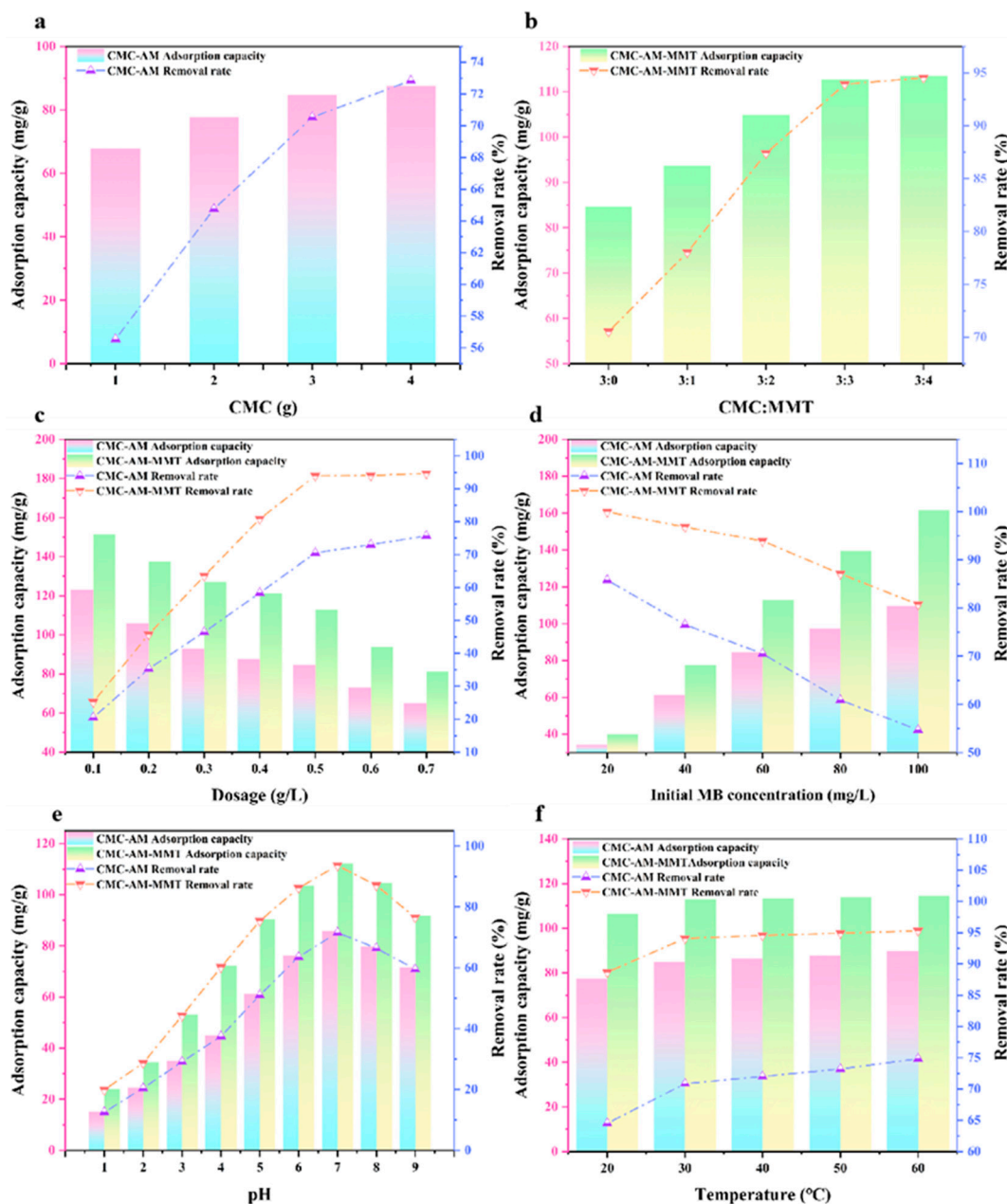


Figure 4. Effect of (a) CMC and (b) MMT components on the adsorption of hydrogel; (c) effect of adsorbent addition amount on adsorption effect of hydrogel; (d) effect of initial concentration of MB on adsorption effect of hydrogel; (e) effect of PH on adsorption of hydrogel; (f) effect of adsorption temperature on adsorption effect of hydrogel.

3.2.2. Dosage of Adsorbent

Figure 4c shows the effect of the dosage of the adsorbent on the adsorption effect of MB. The adsorption efficiency of CMC-AM-MMT hydrogel for MB increased from 25.24% to 95.96%, and the adsorption capacity decreased from 151.44 to 112.75, which was

significantly higher than that of CMC-AM hydrogel without the MMT nanosheets when the amount of hydrogel was in the range of 0.01–0.05 g. The adsorption sites bound to MB were positively correlated with the gel dosage. However, when the adsorption of MB by the gel adsorbent reaches saturation, the increase in its dosage does not improve the adsorption efficiency. Therefore, the optimal dosage of gel adsorbent is 0.05 g.

3.2.3. The Initial Concentration of MB

Figure 4d shows the relationship between different initial MB concentrations and gel adsorption capacity. When the initial concentration of MB was in the range of 20–60 mg/L, the adsorption capacity of CMC-AM-MMT hydrogel for MB increased from 39.99 mg/g to 112.71 mg/g, and the adsorption efficiency decreased slightly from 99.98% to 93.93%, which significantly improved the adsorption effect of CMC-AM hydrogel. The amount of hydrogel adsorbed is proportional to the initial concentration of MB. However, there is an upper limit on the adsorption site of MB for hydrogel adsorbents. When the adsorption site of hydrogel is saturated, the increase in the initial concentration of MB will not affect its adsorption performance. Therefore, in order to obtain higher adsorption efficiency, the optimal initial concentration of MB is 60 mg/L.

3.2.4. pH Effect

Figure 4e illustrates the effect of pH on MB adsorption, showing that the adsorption performance of the hydrogel increases first and then decreases with the increase in pH value. When pH is set to 7, the adsorption capacity of the CMC-AM-MMT hydrogel is 112.33 mg/g, and the adsorption efficiency is 93.61%, which is significantly higher than that of CMC-AM hydrogel. This is because in an acidic environment, H^+ ions are dominant in MB solution, which competes with the cationic dye methylene blue molecules for the active site of the hydrogel adsorbent, which is not conducive to the adsorption of MB by hydrogel. With the increase in pH value, the ionization of the carboxyl group in the hydrogel is beneficial, which greatly promotes the electrostatic interaction between the hydrogel and MB, and its adsorption capacity for MB is therefore enhanced. In an alkaline environment, OH^- in solution could affect the ionization of the carboxyl group in hydrogel, resulting in reduced adsorption capacity.

3.2.5. Adsorption Temperature

Figure 4f shows the effect of temperature on the adsorption properties of hydrogel. It can be seen from the figure that the adsorption amount of MB by hydrogel is positively correlated with temperature. The higher the temperature, the more intense the thermal movement of MB molecules, resulting in increased collision probability between MB molecules and hydrogels, and increased adsorption capacity. However, As the temperature of the solution increases, MB tends to escape from the solid phase. This also indicates that the desorption trend of MB from the boundary to the solution increases with the increase in temperature. Therefore, it is comprehensively considered that the adsorption process of MB by the composite hydrogel is carried out at 30 °C.

3.2.6. Adsorption Kinetics and Internal Particle Diffusion

The kinetic model can be used to understand the rate of the adsorbent adsorption of the solute, and to determine the speed-limiting step and optimal adsorption time in the adsorption process. In order to study the adsorption kinetics of hydrogels, 0.05 g of hydrogel sample was added to 100 mL of methylene blue solution with a concentration of 60 mg/L, and the adsorption amount of methylene blue was measured with time. As shown in Figure 5a, when the hydrogel is placed in methylene blue solution, in the initial adsorption stage, the adsorption capacity of the gel sample to methylene blue increases dramatically. In 2 h, the adsorption capacity of the complex hydrogel approaches the maximum, and then the adsorption rate of the gel gradually slows down until it reaches a stable value. This is mainly due to the micron-scale pore structure of the hydrogel, which

allows MB molecules to quickly move to the interior of the hydrogel and exchange with abundant adsorption sites ($-\text{COOH}$, $-\text{NH}_2$, Na^+ , $-\text{OH}$). It can be seen from Table 2 that the correlation coefficient R^2 of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model is very high, indicating that the composite hydrogel includes physical adsorption and chemical adsorption of MB.

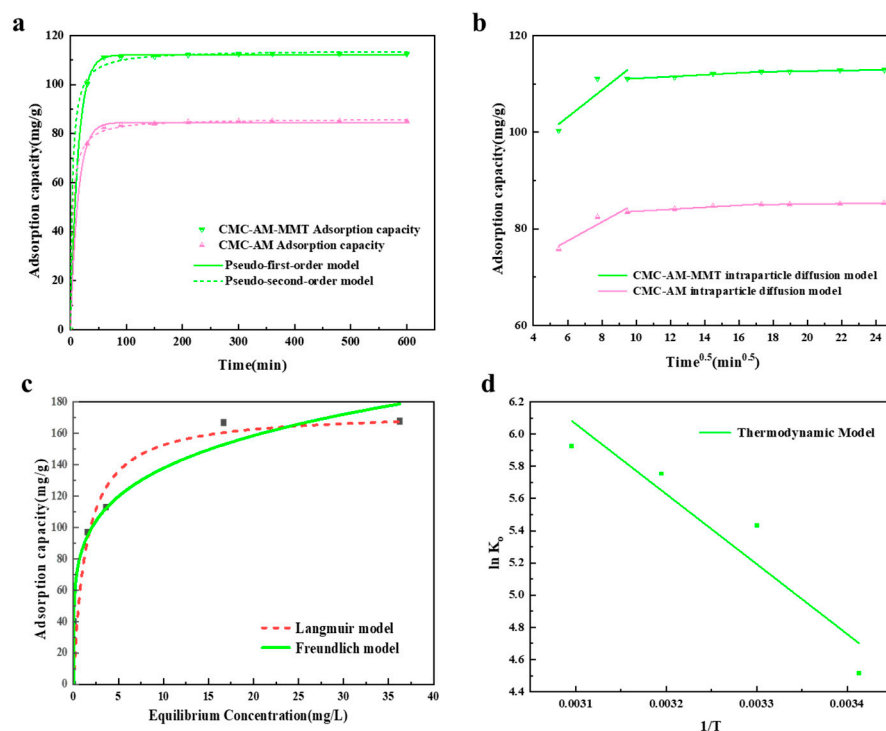


Figure 5. (a) Adsorption kinetics and (b) intraparticle diffusion model of MB removal onto CMC₃-AM and CMC-AM-MMT₃ hydrogel; (c) Isotherm of MB removal onto CMC-AM-MMT₃ hydrogel; (d) Figure of $\ln K_0$ vs. $1/T$ of MB removal onto CMC-AM-MMT₃ hydrogel.

Table 2. The parameters of two kinetic models for the adsorption of MB by hydrogels with different MMT contents.

Initial Concentration	CMC:MMT	Pseudo-First-Order			Pseudo-Second-Order		
		Q_e mg/g	K_1 min^{-1}	R^2	Q_e mg/g	K_2 min^{-1}	R^2
60 mg/L	3:0	84.53	0.0742	0.9993	86.11	0.0032	0.9406
	3:3	112.13	0.0751	0.9998	114.02	0.0026	0.9882

Generally, it is considered that the diffusion of adsorbent in solution can be divided into three stages: from the liquid phase through the boundary layer to the surface of the adsorbent; through the pores to the interior of the particles; and the diffusion of adsorbent at the active site on the surface of the adsorbent. The rate control problem in the reaction was analysed using the Weber and Morris model, which was used to solve the rate constant of hydrogel diffusion. In Figure 5b and Table 3, the fitting results of the Weber and Morris model show that R^2 values are high, and $K_{W\&M1} > K_{W\&M2} > K_{W\&M3}$. The whole adsorption process is mainly composed of three linear parts, indicating that three steps are involved in the adsorption process of MB by CMC-AM-MMT hydrogel. The first stage is the process of MB diffusion from the liquid phase to the hydrogel surface, and the rate is affected by the diffusion rate of MB on the surface. In the second stage, the slope of the fitted line is greatly reduced, which indicates the process of MB diffusion inside the hydrogel particles. The

gentler curve in the third stage is caused by the diffusion of MB inside the pore where the adsorbent is smaller.

Table 3. The parameters of intraparticle diffusion model for the adsorption of MB by hydrogels with different MMT content.

Initial Concentration	CMC:MMT	$K_{W\&M1}$ mg/(g·min)	C mg/g	R^2	$K_{W\&M2}$ mg/(g·min)	C mg/g	R^2	$K_{W\&M3}$ mg/(g·min)	C mg/g	R^2
60 mg/L	3:0	1.952	65.806	0.8965	0.206	81.571	0.966	0.046	84.201	0.958
	3:3	2.789	86.396	0.8366	0.190	109.225	0.951	0.064	111.367	0.942

3.2.7. Adsorption Isotherm

Adsorption isotherm is a model to study the relationship between the adsorption amount of organic pollutants and the concentration of pollutants in solution adsorption materials in a state of equilibrium. For the isothermal adsorption equation of CMC-AM-MMT hydrogel, Langmuir and Freundlich, two typical isothermal adsorption models, were selected to fit and analyse the experimental data. It can be seen from Figure 5c that with the increase in the initial concentration of MB, the adsorption capacity of CMC-AM-MMT hydrogel for dyes shows a trend of increasing and gradually slowing down. This is due to the increase in MB concentration, the increase in the number of dye molecules, and more effective contact with the adsorption site on the CMC surface. The probability of MB colliding with -COOH, -NH₂, -OH and Na⁺ is also greatly increased, and the concentration of MB in the solution is reduced. The speed of adsorption and desorption is increased. However, the adsorption sites on the surface of CMC are limited, and the adsorption of dyes gradually slows down when most of the adsorption sites are occupied. The equilibrium concentration of MB in the solution also moves in a higher direction. Table 4 demonstrates that the correlation coefficient R^2 of the Freundlich isothermal adsorption equation is 0.9676, which is much greater than the correlation coefficient of the Langmuir isothermal adsorption equation. These results support that the adsorption process of MB by composite hydrogels is carried out according to a multilayer adsorption mechanism.

Table 4. The parameters of the Langmuir model and Freundlich model for the adsorption of MB by CMC-AM-MMT hydrogel.

CMC:MMT	Temperature (K)	Langmuir			Freundlich		
		Q_e mg/g	K_L L/mg	R^2	K_F mg/g	n	R^2
3:3	303	173.73	0.0714	0.879	86.4023	4.9443	0.9676

3.2.8. Thermodynamic Parameters

The adsorption thermodynamics of MB by hydrogel at an adsorption temperature of 2 °C to 50 °C were studied. In Figure 5d and Table 5, ΔG° is shown to be negative at all temperatures, which indicates that the adsorption process of MB on the hydrogel is spontaneous. The positive value of ΔH° indicates that the adsorption process is endothermic. The adsorption capacity of MB increased with the increase in temperature. In general, the ΔH° value of physical adsorption is between 2.1 and 20.9, and the ΔH° value of chemical adsorption is between 80 and 200 kJ·mol^{−1} [55]. The ΔH° value of MB adsorption on hydrogel is neither in the range of physical adsorption nor chemisorption, indicating that the adsorption of MB by hydrogel also involves other adsorption processes, such as electrostatic interaction. The ΔS° value of the adsorption of cations by hydrogel is positive, indicating that the degree of disorder and randomness of the solid–solution interface increase after adsorption. The thermodynamic calculation results show that the hydrogel prepared under the present experimental conditions can be used as the adsorbent of MB, and can effectively remove MB from aqueous solution at ambient temperature.

Table 5. Thermodynamic parameters for the adsorption of MB by CMC-AM-MMT hydrogel.

Thermodynamic Constant	Temperature (K)			
	293	303	313	323
K_o	91.35	228.60	315.21	373.75
$\Delta G^\circ (\times 1000 \text{ kJ mol}^{-1})$	−10.99	−13.68	−14.97	−15.90
$\Delta H^\circ (\times 1000 \text{ kJ mol}^{-1})$	36.14	36.14	36.14	36.14
$\Delta S^\circ (\text{J mol}^{-1} \text{ K}^{-1})$	162.44	162.44	162.44	162.44

3.3. Cr^{6+} Ions Removal Performance

3.3.1. Initial CMC and MMT Content

Figure 6a,b shows the effects of CMC-AM-MMT hydrogels prepared with different CMC and MMT addition amounts on the adsorption capacity and removal rate of Cr^{6+} . It can be seen from the figure that when MMT is not added and the amount of AM is constant, the adsorption capacity of hydrogel is proportional to the amount of CMC added. This is due to the increase in CMC content, and the carboxyl group inside the gel chelates with Cr^{6+} . When the amount of CMC increases to a certain extent, although the number of carboxyl groups increases, the gel volume is limited, and its internal pores are compressed, which affects the adsorption amount and removal rate of Cr^{6+} by the gel. When the amount of MMT and AM is constant, the adsorption capacity of hydrogel is also positively correlated with the amount of MMT. This is because MMT acts as the skeleton structure of the hydrogel, which increases the porosity of the gel and thus improves the adsorption capacity of the gel. When the amount of MMT reaches a certain extent, the pores of the gel cannot continue to expand, and the adsorption capacity of Cr^{6+} cannot be enhanced. Therefore, when the amount of CMC is 3 g and the amount of CMC:MMT is 1:1, the adsorption performance of CMC-AM-MMT hydrogel is better. Further adsorption experiments were carried out with $\text{CMC}_3\text{-AM}$ and CMC-AM-MMT_3 hydrogel.

3.3.2. Dosage of Adsorbent

Figure 6c shows the influence of the dosage of hydrogel adsorbent on the adsorption effect of Cr^{6+} . When the amount of hydrogel is in the range of 0.1–0.5 g, the adsorption efficiency of CMC-AM-MMT hydrogel for Cr^{6+} increases from 31.69% to 67.45%, and the adsorption capacity decreases from 3.17 to 1.35, which shows a great improvement compared with the adsorption effect of CMC-AM hydrogel. This is because the amount of hydrogel adsorbents continues to increase, and the active site is able to bind to Cr^{6+} , so the adsorption efficiency increases. When the adsorption of Cr^{6+} by the adsorbent reaches saturation, the increase in its dosage does not improve the adsorption efficiency. Therefore, the optimal dosage of gel adsorbent is 0.5 g.

3.3.3. Initial Concentration of Cr^{6+}

Figure 6d shows the relationship between different initial Cr^{6+} concentrations and gel adsorption effect. When the initial concentration of Cr^{6+} is in the range of 5–10 mg/L, the adsorption capacity of Cr^{6+} by CMC-AM-MMT hydrogel increases from 0.69 mg/g to 1.33 mg/g, and the adsorption efficiency decreases from 69.02% to 66.66%, which is significantly higher than the adsorption effect of CMC-AM hydrogel. The amount of hydrogel adsorbed is proportional to the initial concentration of Cr^{6+} . However, there is an upper limit on the adsorption site of Cr^{6+} for hydrogel adsorbents. When the adsorption site of hydrogel is saturated, the initial concentration of Cr^{6+} does not increase the adsorption efficiency of hydrogel. Therefore, in order to obtain higher adsorption efficiency, the optimal initial concentration of Cr^{6+} is 10 mg/L.

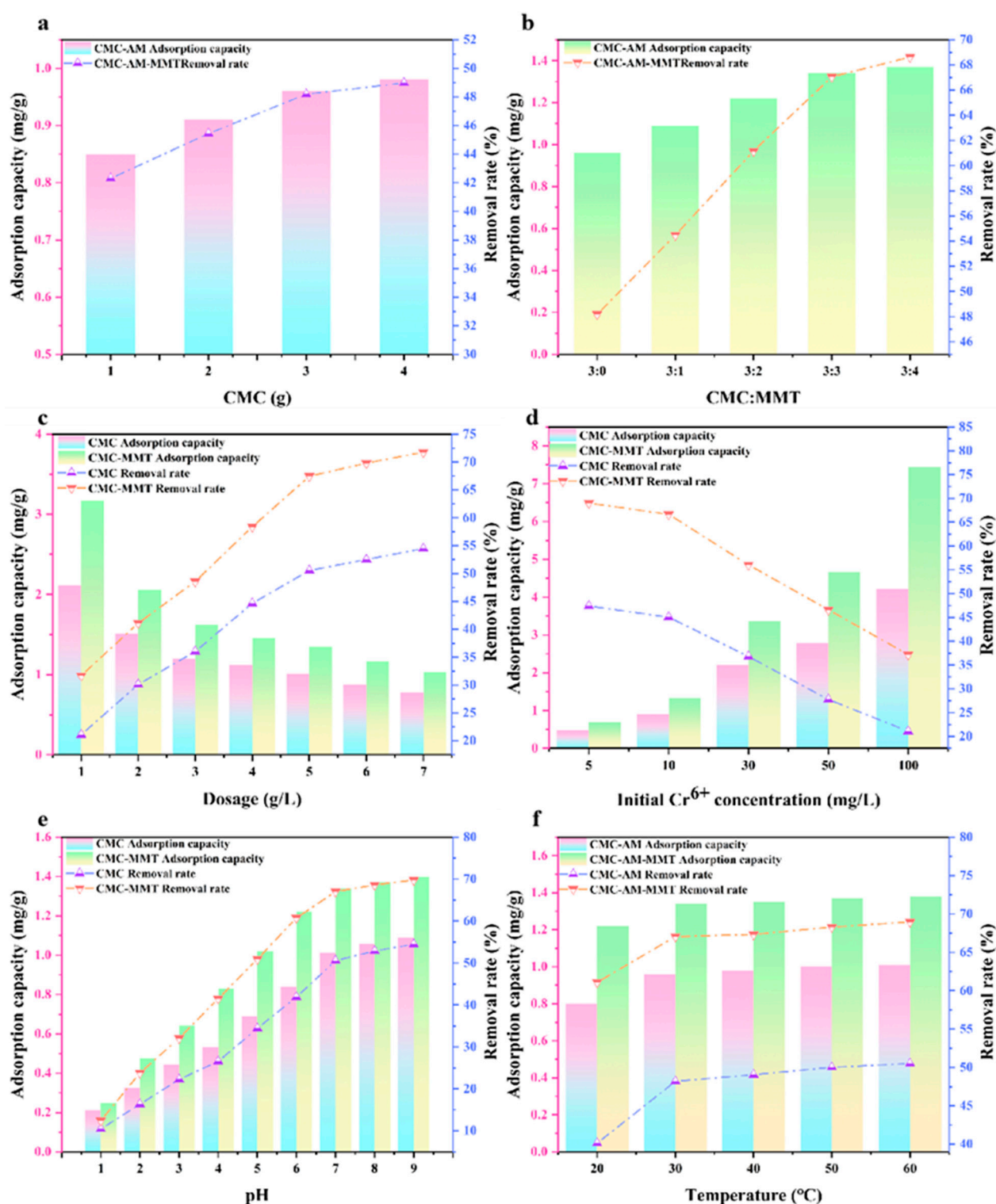


Figure 6. Effect of (a) CMC and (b) MMT components on the adsorption of hydrogel; (c) Effect of adsorbent addition amount on adsorption effect of hydrogel; (d) Effect of initial concentration of Cr^{6+} on adsorption effect of hydrogel; (e) Effect of PH on adsorption of hydrogel; (f) Effect of adsorption temperature on adsorption effect of hydrogel.

3.3.4. pH Effect

Figure 6e shows the influence of different pH values on the adsorption effect of Cr^{6+} . As can be seen from the figure, as the pH increases from 1 to 7, the adsorption capacity of

hydrogel increases from 0.24 mg/g to 1.34 mg/g, and the adsorption efficiency increases from 12.44% to 67.05, which is significantly higher than that of CMC-AM hydrogel. This is due to the large amount of H^+ and H_3O^+ in the Cr^{6+} solution competing with Cr^{6+} as the active site of the hydrogel adsorbent in the acidic environment. With the increase in pH, the concentration of H^+ decreased, which was conducive to the adsorption of hydrogel. In an alkaline environment, the OH^- in the solution will combine with Cr^{6+} to form a precipitate. Therefore, when the pH is 7, the gel has the best adsorption effect on Cr^{6+} .

3.3.5. Adsorption Temperature

Figure 6f shows the effect of temperature on the adsorption properties of hydrogel. It can be seen from the figure that the adsorption amount of Cr^{6+} by hydrogel is positively correlated with temperature. The higher the temperature, the stronger the thermal motion of Cr^{6+} , the greater the probability of collision with hydrogel, and the greater the adsorption capacity. With the increase in temperature, the solubility of the adsorbent increases, which makes the interaction between adsorbent and solvent stronger than the interaction between adsorbent and adsorbate. The curve flattens out. Therefore, the adsorption process of Cr^{6+} by hydrogel is most favourable at 30 °C.

3.3.6. Adsorption Kinetics and Internal Particle Diffusion

In order to study the adsorption kinetics of hydrogels on Cr^{6+} , 0.5 g of the hydrogel samples was added to 100 mL of Cr^{6+} solution with a concentration of 10 mg/L. The adsorption amount of Cr^{6+} was identified. The rapid adsorption rate of hydrogels at the initial stage of adsorption is related to the tightly connected porous three-dimensional network structure and ion exchange adsorption of hydrogel. When the adsorption site is occupied by Cr^{6+} molecules, the surface transport capacity of the pore is blocked, and the adsorption reaches an equilibrium state. It can be seen from Table 6 that the correlation coefficient R^2 of the pseudo-first-order kinetic model is high, indicating that physical adsorption takes place for the composite hydrogel when removing Cr^{6+} ions.

Table 6. The parameters of two kinetic models for the adsorption of Cr^{6+} by hydrogel with different MMT contents.

Initial Concentration	CMC:MMT	Pseudo-First-Order			Pseudo-Secondary		
		Q_e mg/g	K_1 min^{-1}	R^2	Q_e mg/g	K_2 min^{-1}	R^2
10 mg/L	3:0	0.95	0.0485	0.9972	0.99	0.1124	0.9313
	3:3	1.31	0.0055	0.9716	1.39	0.0423	0.9408

The internal diffusion model is usually used to study the transfer process and chemical reaction mechanism in adsorption. As shown in Figure 7b and Table 7, the Weber and Morris model has a high degree of fitting. Because $K_{W\&M1} > K_{W\&M2} > K_{W\&M3}$, the fitting curve of the internal diffusion of the particle can be divided into three linear parts, indicating that the adsorption process consists of three stages. The first stage is the diffusion of Cr^{6+} from the solution to the surface of the hydrogel. In the second stage, Cr^{6+} passes through the boundary layer of the hydrogel and reacts with the adsorption sites in the hydrogel, which belong to the internal diffusion of particles. In the third stage, the particles reach the micropores and react further with the adsorption sites in the hydrogel. Since the fitting curves of these three stages do not pass through the origin of coordinate axes, this indicates that the adsorption process is controlled by boundary layer diffusion and internal diffusion.

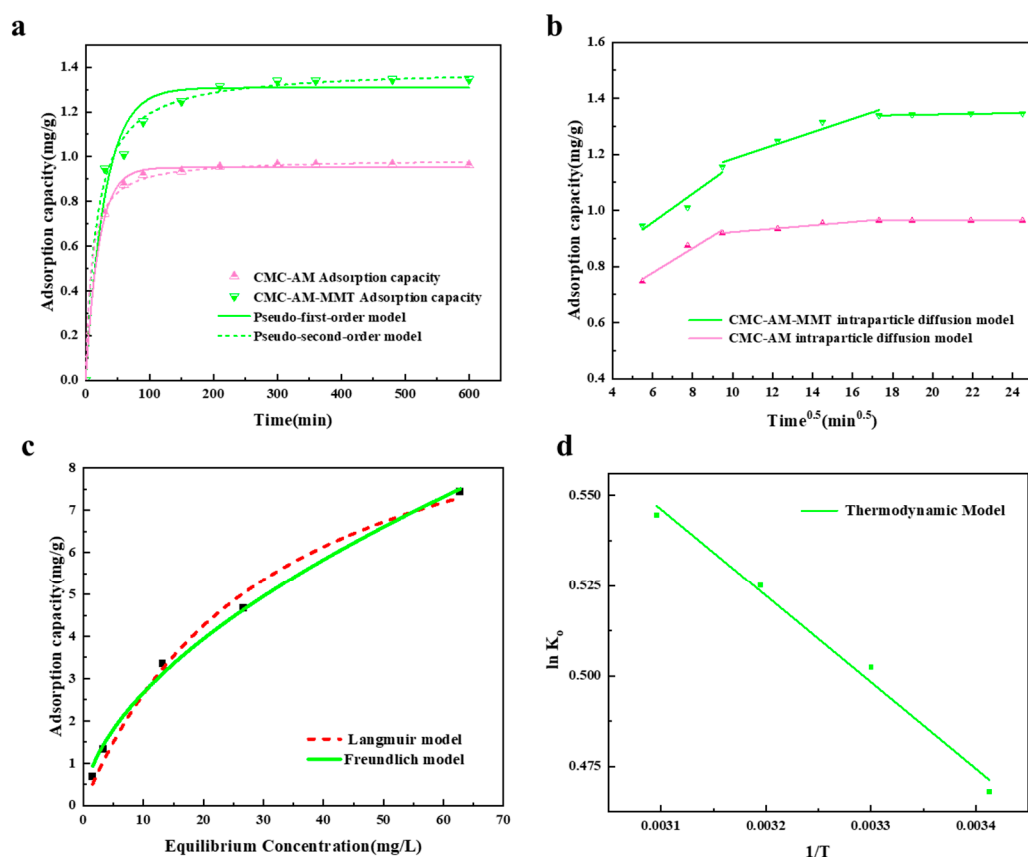


Figure 7. (a) Adsorption kinetics and (b) intraparticle diffusion model of Cr^{6+} removal onto CMC₃-AM and CMC-AM-MMT₃ hydrogel; (c) isotherm of Cr^{6+} removal onto CMC-AM-MMT₃ hydrogel; (d) figure of $\ln K_0$ vs. $1/T$ of Cr^{6+} removal onto CMC-AM-MMT₃ hydrogel.

Table 7. The parameters of the intraparticle diffusion model for the adsorption of Cr^{6+} by hydrogels with different MMT contents.

Initial Concentration	CMC:MMT	$K_{W\&M1}$ mg/(g·min)	C mg/g	R^2	$K_{W\&M2}$ mg/(g·min)	C mg/g	R^2	$K_{W\&M3}$ mg/(g·min)	C mg/g	R^2
10 mg/L	3:0	0.0438	0.515	0.9605	0.0145	0.862	0.9738	0.0061	0.963	0.9526
	3:3	0.0512	0.650	0.9141	0.0237	0.947	0.9329	0.0011	1.320	0.8922

3.3.7. Adsorption Isotherm

Two isothermal adsorption models of Langmuir and Freundlich were applied to fit and analyse the experimental data for Cr^{6+} ion adsorption. It can be seen from Figure 7c that with the increase in the initial concentration of Cr^{6+} , the adsorption capacity of CMC for dyes shows a trend of increasing and then gradually slowing down. The adsorption process mainly relies on the exchange of $-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$ and Na^+ on the CMC surface. From Table 8, it can be seen that the correlation coefficient R^2 of the Freundlich isothermal adsorption equation is 0.9913, which is slightly greater than the correlation coefficient of Langmuir isothermal adsorption model, which shows that the adsorption process of Cr^{6+} by the composite hydrogel is performed predominantly through a multilayer adsorption mechanism.

Table 8. The parameters of the Langmuir model and Freundlich model for the adsorption of Cr^{6+} by CMC-AM-MMT hydrogel.

CMC:MMT	Temperature (K)	Langmuir			Freundlich		
		Q_e mg/g	K_L L/mg	R^2	K_F mg/g	n	R^2
3:3	303	10.95	0.0318	0.9564	0.73	1.7771	0.9931

3.3.8. Thermodynamic Parameters

The adsorption thermodynamics of Cr^{6+} on hydrogel were studied at 20 °C to 50 °C, and the obtained thermodynamic parameters of Cr^{6+} adsorption on hydrogel are shown in Figure 7d and Table 9. The positive value of ΔS° indicates that the randomness of the solid solution interface increases irregularly during the adsorption of Cr^{6+} on the hydrogel. ΔG° is negative at all temperatures, indicating the feasibility of Cr^{6+} adsorption on hydrogel and the spontaneity of the adsorption process. The ΔH° value of Cr^{6+} adsorbed on hydrogel is very low, which indicates that the influence of temperature on the adsorption of Cr^{6+} is negligible. On the other hand, it shows that the adsorption process is a physical adsorption process, which is consistent with the results of adsorption kinetics. This confirmed that the adsorption mechanism of Cr^{6+} on hydrogel includes the existence of weak interaction between the hydrogel surface groups and Cr^{6+} surface.

Table 9. Thermodynamic parameters for the adsorption of Cr^{6+} by CMC-AM-MMT hydrogel.

Thermodynamic Constant	Temperature (K)			
	293	303	313	323
K_o	1.59	1.65	1.69	1.72
ΔG° ($\times 1000$ kJ mol $^{-1}$)	−1.14	−1.26	−1.36	−1.46
ΔH° ($\times 1000$ kJ mol $^{-1}$)	1.98	1.98	1.98	1.98
ΔS° (J mol $^{-1}$ K $^{-1}$)	10.70	10.70	10.70	10.70

4. Conclusions

A novel type of cellulose-based hydrogel material is fabricated as an adsorbent for contaminant removal in wastewater via chain radical polymerization and a freeze-drying process. The incorporation of MMT nanosheets can significantly enhance the organic dye and metal ion adsorption of hydrogel, benefiting from the rigid support of the hydrogel skeleton and providing an active adsorption site for containment removal. The optimal mass ratio of CMC to MMT for the adsorption performance of the hydrogel is verified to be 1:1. The optimal adsorption conditions of CMC-AM-MMT hydrogel for MB are as follows: an initial concentration of MB 60 mg/L, pH 7, a adsorbent dosage of 0.5 g/L, an adsorption temperature of 30 °C, and an adsorption capacity of 112.9 mg/g. The optimal adsorption conditions of CMC-AM-MMT hydrogel for Cr^{6+} are as follows: an initial concentration of Cr^{6+} 10 mg/L, pH 7, an adsorbent dosage of 5 g/L, and an adsorption capacity of 1.35 mg/g. The fitting results of the isothermal models, the kinetic models, internal particle diffusion models and thermodynamics of the experimental data of the adsorbate adsorption process show that the adsorption of MB by hydrogel is a spontaneous segmented process of multi-layer physical and chemical adsorption. Additionally, the adsorption of Cr^{6+} ions by hydrogel is a spontaneous segmented process of multi-layer physical adsorption. The CMC-AM-MMT hydrogel has the advantages of simple preparation, non-toxicity, low cost, good biocompatibility, and environmental friendliness. However, the removal effect of CMC-AM-MMT hydrogel on heavy metal ions is not very satisfactory. Hydrogels with multiple adsorption functions and deeper mechanisms of hydrogel adsorption are being explored, and further facile modification approaches for improving the adsorption performance of cellulose-based materials should be developed.

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