

Article

Preparation of Sulfhydryl Functionalized MCM-48 and Its Adsorption Performance for Cr(VI) in Water

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Abstract: In this study, we modify the Mobil Composition of Matter No. 48 (MCM-48) silica material (MCM-48-SH) using Mercapto. The preparation conditions of MCM-48-SH are then explored, its structural characteristics are analyzed using characterization, and it is used to adsorb Cr(VI) from wastewater. A series of experiments are then designed to adsorb Cr(VI) in experimental water, and the influence of solution environment changes (such as time, temperature, pH, and coexisting ions) on the adsorption effect was explored. The experimental data showed that the MCM-48-SH material not only retained the basic structure of MCM-48 but also successfully grafted the functional group -SH. The adsorption of Cr(VI) on MCM-48-SH followed the Langmuir isotherm model and the kinetic adsorption was fitted with a pseudo-second-order kinetic model. Under these conditions, the adsorption capacity of MCM-48-SH (17.9 mg/g) on Cr(VI) was much larger than that of unmodified MCM-48 (4.0 mg/g) and amino-modified MCM-48-NH₂ (0.5 mg/g). The adsorption effect was the most obvious when the pH = 2 but the adsorption effect was not good under alkaline conditions. Other competitive ions in the solution had an influence on the adsorption effect, among which anions had a great influence. Within 3 d, when the concentration of Cr(VI) was 80 mg/L, the maximum adsorption capacity reached 17.9 mg/g and the maximum removal rate reached 93.45%. In the comparative adsorption experiment, the adsorption effect of MCM-48-SH (17.9 mg/g) on Cr(VI) was notably better than that of the other two common adsorbents: coconut shell activated carbon (9.2 mg/g) and bentonite (1.2 mg/g). In summary, MCM-48-SH can be used to effectively eliminate Cr(VI) in waste water.



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1. Introduction

Hexavalent chromium, or Cr(VI), is an ingested poison. In addition, skin contact may lead to sensitivity and genetic defects. Inhalation may cause cancer and pose a lasting danger to the environment [1,2]. In 2013, in a report on the toxicity of hexavalent chromium prepared by the World Health Organization (WHO) [3], Cr(VI) was classified as a genotoxic substance, and when its concentration in drinking water reaches 0.3 µg/L it poses a risk to the human body. In July 2019, Cr(VI) compounds were listed in the first batch of toxic and harmful water pollutants by China [4].

Owing to its corrosion resistance, Cr(VI) is used in many industries such as leather tanning, the electronic industry, and electroplating production [5–7]. During the industrial production of chromium, a lot of chromium slag and other waste gases and wastewater are produced [8]. Cr(VI) dissolves in water and leaches to the surface, affecting water resources, soil, farmland, and human health through water and soil transport [2]. In long-term research [1,9–11], scholars have studied various removal methods for hexavalent chromium ions in water, such as adsorption, anion exchange, reverse osmosis membrane, and reduction–coagulation–filtration (RCF). However, the cost of the anion exchange method is high, the membrane technology is facing the problem of membrane pollution,

and the RCF process is difficult to utilize at a large scale, while the adsorption method is simpler and more effective.

Compared with anion exchange and membrane technology, the typical adsorption method [12] has the advantages of high efficiency, low cost, environmental friendliness, a recyclable adsorbent, and simple operating conditions, and has been applied in many industrial processes [13–15] including synthetic polymers, silica, graphene, activated carbon, and biosorbents for the adsorption of Cr(VI). Nanomaterials have high specific surface areas and porosities [16]. Scholars have been exploring their applications in catalysis, electrochemistry, water treatment, pharmacy, and biology [17–22]. Nanomaterials are functionalized using organic and inorganic acids, bases and alkaline solutions, and many other mineral and organic compounds in order to develop materials with physicochemical properties such as carbon nanomaterials [23], metal oxide nanomaterials [24], silica nanomaterials [25], and organic nanomaterials [26]. Among these, modified mesoporous materials have more active adsorption sites and dominant surface groups [27]. Hence, the adsorption efficiency of a pollutant is improved. Compared with traditional materials, mesoporous materials, as effective adsorbents during water treatment, have a unique structure and excellent performance.

MCM-48, as a typical pure cubic mesoporous silica material, has the characteristics of a large specific surface area and a high degree of order, and these characteristics are different from two-dimensional mesoporous materials such as MCM-41 and SBA-15 [21]. The internal channels of MCM-48 are composed of two sets of mutually independent three-dimensional spiral channel network structures. Due to its unique structure, MCM-48 has good long-range periodicity, a stable skeleton, and good transmission performance, and is easy to functionalize to the surface of materials. MCM-48 is widely used in the field of adsorption and separation of macromolecules in water.

Currently, functional groups have a good effect on the separation of various ions in water, such as the removal of Pb^{2+} by NH_2 , the removal of Ca^{2+} and Co^{2+} by $-\text{COOH}$, the removal of Pb^{2+} by $[-\text{P}=\text{O}(\text{OH})_2]$, and the removal of Nd (III) by graphene oxide [28–31]. In 2015, Helbling and Dichtel found that the porous β -cyclodextrin polymer material obtained by cross-linking β -cyclodextrin with rigid aromatic groups can quickly remove organic pollutants in water and significant progress has been made [32]. Its adsorption rate constant was 15–200 times that of activated carbon. In 2019, the Bhavna A. research group adopted the grafting of the functional group ethylenediamine cyanurate [10], making progress in adsorbing Cr(VI) from water.

Compared with other functional groups, the $-\text{SH}$ group is very effective for the removal of heavy metal ions from water, such as Hg^{2+} and Zn^{2+} [33,34]. In 2009, Delacôte et al. modified $-\text{SH}$ on MCM-48 to achieve Hg^{2+} well adsorption [33]; in 2014, Anbia et al. magnetically modified MCM-48 and removed Pb(II), Cu(II), Cr(VI), and Cd(II) [35]; in 2012, Marjanović et al. modified seafoam with amine and autumn to achieve Cr(VI) adsorption [36]; and in 2021, Shuangyou Bao's group grafted 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole groups onto graphene oxide as Cr(VI) and Hg^{2+} adsorbents [37], wherein a maximum removal rate of 99.9% was achieved. These results indicate that $-\text{SH}$ has an adsorption effect on heavy metal ions in water and can be used as a functional group to modify MCM-48 and adsorb Cr(VI) in water.

In this study, we combine other scholars' research on the removal of Cr(VI) [38–42] and a functionalized group $-\text{SH}$ is grafted onto the surface of MCM-48 by chemically modifying silanol on the surface of MCM-48. This new mesoporous adsorbent, MCM-48-SH, is prepared and compared with other mesoporous materials in many dimensions. Following this, its ability to adsorb Cr(VI) is evaluated. The purpose of this study is to study whether $-\text{SH}$ on the silanol surface of a grafted material will improve the adsorption effect of MCM-48 and determine whether MCM-48-SH can adsorb Cr(VI) better than MCM-48- NH_2 . In addition, MCM-48-SH, a new mesoporous adsorbent material, is compared with coconut shell activated carbon (CAC) and bentonite (BTT), which are the traditional heavy metal adsorbent materials, to explore the practical adsorption performance of MCM-48-SH.

2. Materials and Methods

2.1. Experimental Raw Materials

The reagents used in the synthesis of material in this experiment were all of analytical purity. The following reagents were purchased from Sigma-Aldrich (Co.St.Louis, MO, USA): tetraethyl orthosilicate (TEOS) (CAS: 78-10-4, 98% purity, molar mass 208.33 g/mol), 3-mercaptopropyl ethoxysilane (MPTMS) (CAS: 4420-74-0, 95% purity, molar mass 196.34 g/mol), cetyltrimethylammonium bromide (CTAB) (CAS: 57-09-0, 99% purity, molar mass 364.45 g/mol), and 3-aminopropylethoxysilane (APTMS) (CAS: 13822-56-5, 97% purity, molar mass 179.29 g/mol). The other experimental reagents were purchased from the Sinopharm Pharmaceutical Company (Beijing, China). The standard solution used in the experiment was purchased from the National Standard Material Center (hexavalent chromium standard solution in water) to provide Cr(VI).

2.2. Preparation of the Adsorption Materials

The MCM-48 was prepared according to methods previously published in the literature [27,43]. The MCM-48-SH was prepared using the co-shrinkage method [44]. With CTAB [45] as the template and TEOS and MPTMS as the silicon sources, the CTAB, NaOH solution, and deionized water were mixed at a ratio of 0.8 g: 2 mL: 32 mL and then stirred at room temperature at 500 r/min. After that, the stirring rate was increased to 1000 r/min, and 2 mL TEOS and 1 mL MPTMS were added dropwise. This was stirred at room temperature at 500 r/min for 1 h, and then the milky white mixture was immediately transferred into a 100 mL tetrafluoroethylene liner. This was placed in a high-pressure reaction kettle, sealed, and crystallized at 105 °C for 3 d. After crystallization, the high-pressure reaction kettle was cooled to room temperature. The mixed liquid was taken out, filtered using a Brinell funnel, washed with methanol and acetone under reflux for 48 h to remove the surfactant, then washed with deionized water to neutrality, and dried at low temperature. The product obtained after drying was MCM-48-SH. MCM-48-NH₂ was prepared for the comparative experiment, and TEOS and APTMS were used as the double silicon sources. The other synthesis processes were the same.

CAC [46] and BTT [47] were ground and sieved with a 200-mesh sieve, and then deionized water was added to them. The mixture was ultrasonicated for 0.5 h to remove the supernatant. A total of 500 mL of a 0.01 M NaOH solution was added to the deposited solids and this was stirred evenly, placed on a heating plate, boiled at 100 °C, and refluxed for 1.5 h. Deionized water was then utilized to filter and clean them until the CAC and BTT were neutral. They were then dried at a low temperature for later use.

2.3. Adsorption Experiment

To explore the adsorption properties of MCM-48-SH, a number of experiments were designed.

To study the adsorption effect of MCM-48-SH, 100 mg MCM-48, MCM-48-SH, and MCM-48-NH₂ were added to Cr (VI) solution ($c = 80$ mg/L, $\text{pH} = 2$, $t = 25$ °C) and stirred for 3 d to fully react; the maximum adsorption capacity of the material was investigated under optimal reaction conditions.

In the adsorption equilibrium experiment, 25 mg of adsorbent (MCM-48, MCM-48-SH) was added to 50 mL of Cr (VI) solution ($\text{pH} = 2$, $t = 25$ °C) prepared with different initial concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/L) and stirred for 3 d to fully react. The concentration of Cr (VI) solution was measured after adsorption and the adsorption capacities of adsorbents MCM-48, MCM-48-SH, and MCM-48-NH₂ were calculated.

The effects of the solution environment on the adsorption performance of MCM-48-SH were studied from three aspects: the solution pH, the metal cations, and the anions. Different solution pH values and the coexisting ionic solution environments were designed and the effects of the above factors on the adsorption of Cr(VI) were evaluated. The concentration was measured, and the effects of the different solution environments on the adsorption properties of MCM-48-SH were investigated.

In comparison with other adsorbents, different adsorbents (MCM-48-SH, CAC, BTT) were added to 100 mL of the Cr(VI) solution and the initial concentration was the best adsorption concentration in the experiment. These were stirred at 25 °C for 3 d. The concentration of Cr(VI) in the solution was measured and compared to the concentration changes of the Cr(VI) solution under the different adsorbents.

2.4. Detection and Analysis Methods

The detection and characterization methods used in the experiment are described in the Supplementary Materials.

The Langmuir and Freundlich models were utilized in this study [48], as well as the pseudo-first-order kinetic model and the pseudo-second-order kinetic model [49]. The above model was used to study the phase adsorption mechanism of the adsorbents and Cr(VI) ions.

3. Results and Discussion

3.1. MCM-48-SH Characterization and Analysis of Materials

3.1.1. Scanning Electron Microscope (SEM) Characterization Analysis

The SEM photographs of MCM-48-SH, MCM-48, CAC, and BTT are shown in Figure 1. The microstructure and morphology of the adsorbents were imaged using SEM. The mesoporous material MCM-48-SH, prepared in this experiment, was approximately spherical with an average diameter of approximately 2 μm and a uniform particle size. The SEM photos of MCM-48 showed that the material was formed by uniform nanoparticles and the particle size distribution was very tight, which indicated a good synthesis process. The SEM photographs of the CAC and BTT showed that the coconut shell activated carbon had a tubular structure, an irregular hexagonal shape, and many broken surfaces. The bentonite had a lamellar structure with an irregular distribution, an uneven particle size distribution, and no specific shape.

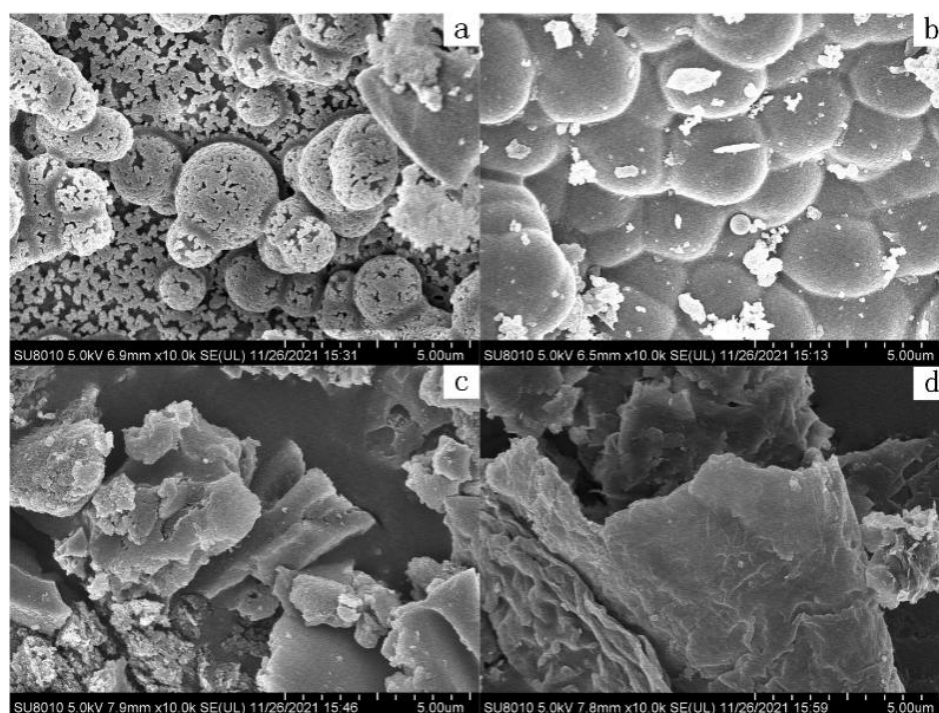


Figure 1. SEM images of: (a) MCM-48-SH, (b) MCM-48, (c) CAC, and (d) BTT. SEM, scanning electron microscope; CAC, coconut shell activated carbon; BTT, bentonite.

Compared with MCM-48's spherical or elliptical shape and uniform size [50], the structure of MCM-48-SH was more irregular than MCM-48. This indicated that due to the

grafting of the sulfhydryl groups on the surface of the MCM-48, the silica double helix pore skeleton of MCM-48-SH was slightly disrupted, resulting in a decrease in the order and particle size uniformity of MCM-48-SH [27,51]. Compared with CAC and BTT, the pore structure of MCM-48-SH was more obvious, the morphology was more regular, the microscopic scale was smaller, and the spherical porous structure of the ball had a higher specific surface area and an open pore structure. In addition, the surface chemistry and other characteristics of the material were more conducive to Cr(VI) adsorption on the material surface.

3.1.2. X-ray Diffraction (XRD) Characterization Analysis

The XRD measurements of MCM-48, MCM-48-SH, and MCM-48-NH₂ were conducted to determine the order of the material. The XRD pattern is shown in Figure 2. According to the image, MCM-48-SH had three diffraction peaks of 100, 110, and 200 in the small-angle diffraction peak spectrum. According to the XRD pattern, the out-of-plane spacing $d_{100} = 7.005$ nm and the unit cell parameter $a_0 = 8.090$ nm were calculated.

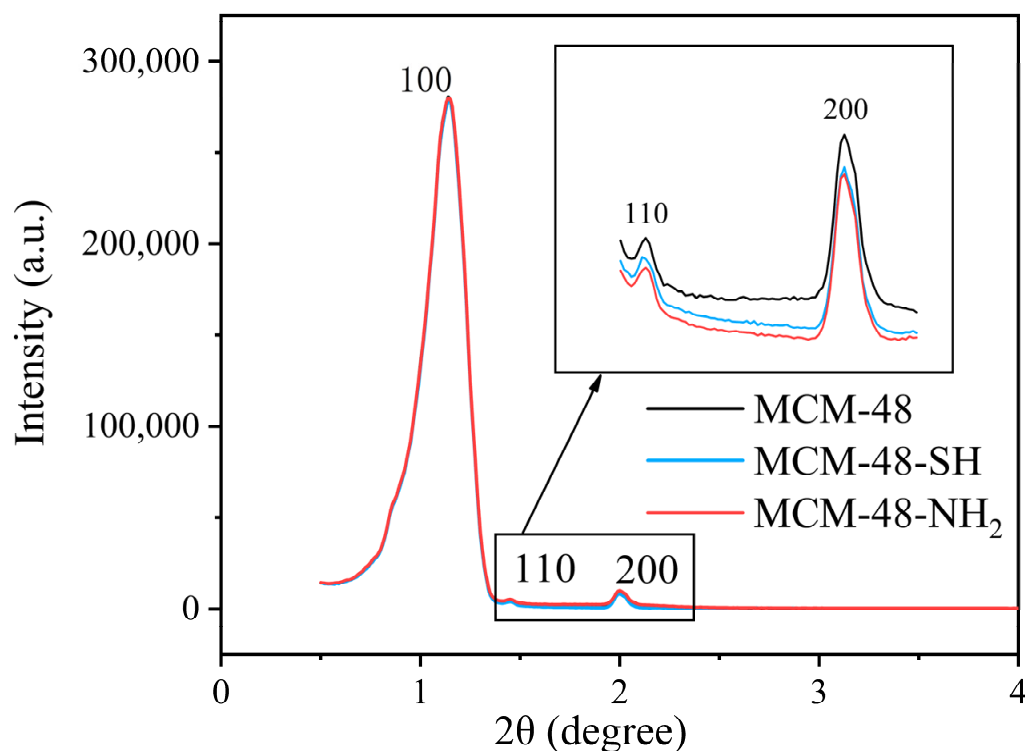


Figure 2. XRD spectra of MCM-48-SH, MCM-48, and MCM-48-NH₂.

The XRD pattern analysis of MCM-48-SH was compared with that found in previous studies [52,53]. In contrast, the small-angle diffraction characteristic spectrum confirmed that MCM-48-SH has the structural characteristics of MCM-48 mesoporous materials. However, compared with the diffraction patterns of typical mesoporous materials, the characteristic absorption peak intensity decreased, which indicated that the introduction of the sulfhydryl groups had an impact on the ordered structure of the mesoporous materials. In addition, the pore size decreased, resulting in an increase in the lattice defects that finally led to a decrease in the diffraction peak intensity and material order. Combined with the SEM image of MCM-48-SH, this was consistent with the structural characteristics reflected by the XRD pattern data and this mutually confirmed the typical mesoporous structure of MCM-48-SH.

3.1.3. Brunauer–Emmett–Teller (BET) Characterization Analysis

According to the BET characterization results (Table 1; Figures 3 and 4), the specific surface area and average pore diameter of MCM-48-SH and MCM-48-NH₂ were lower than those of MCM-48, and this was due to the influence of the grafting of surface functional groups on the ordered mesoporous structure [13]. In general, the larger the specific surface area and pore size, the more favorable the material was for the adsorption of pollutants. A small pore size prolongs the time for the target ions to diffuse into the interior of the pore channel and achieve adsorption, which is not conducive to ion entry into the pore channel. This results in a longer adsorption equilibrium time and less effective adsorption. MCM-48-SH had a greater adsorption capacity for Cr(VI) than MCM-48, primarily due to the introduction of sulfhydryl groups resulting in more functional groups on the outer surface of the material and within the pore channel, as well as more adsorption sites. The rapid increase in the adsorption capacity at $0.25 < P/P_0 < 0.36$ confirmed the existence of the mesoporous structure of MCM-48-SH. At $0.36 < P/P_0 < 0.99$, the adsorption termination platform appeared, and no further multi-layer adsorption occurred. These results indicated that the N₂ adsorption isotherm of MCM-48-SH was type IV, with capillary coalescence of the adsorbate occurring and a rapid rise in the isotherm. When all mesopores coalesced, adsorption occurred only on the external surfaces that were much smaller than the pore surface area and the curve was flat. Adsorption on larger pores at relative pressures near to one further suggested that MCM-48-SH was a small pore size mesoporous adsorbent material.

Table 1. Specific surface area, average pore diameter, and average pore volume of MCM-48, MCM-48-SH, and MCM-48-NH₂.

Material	Specific Surface Area (m ² /g)	Mean Pore Size (nm)	Average Pore Volume (cm ³ /g)
MCM-48	951.493	5.167	0.746
MCM-48-SH	596.396	4.003	0.623
MCM-48-NH ₂	348.296	2.295	0.669

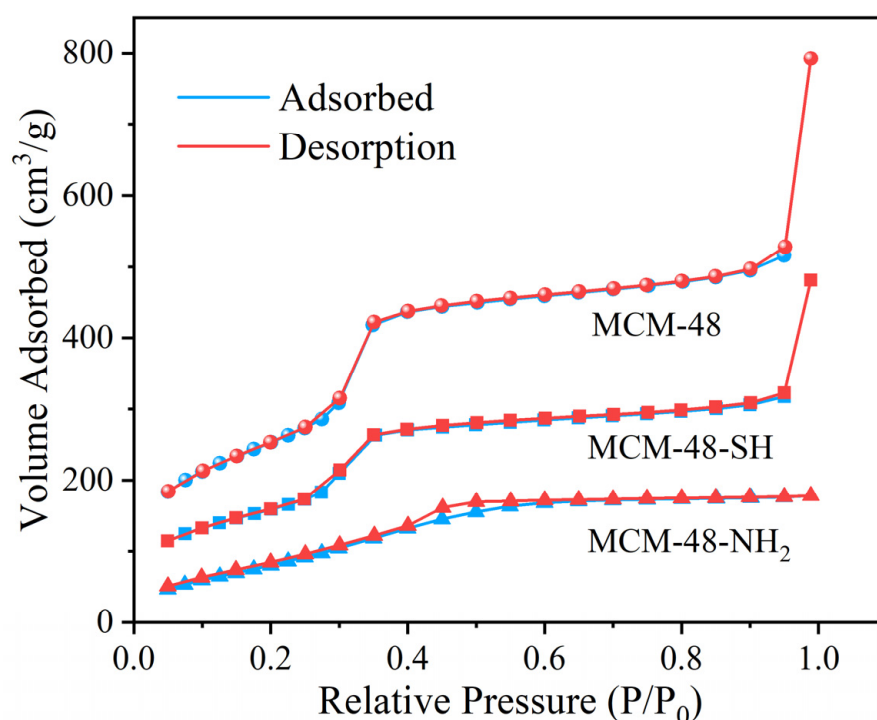


Figure 3. N₂ adsorption–desorption diagram of MCM-48-SH, MCM-48, and MCM-48-NH₂.

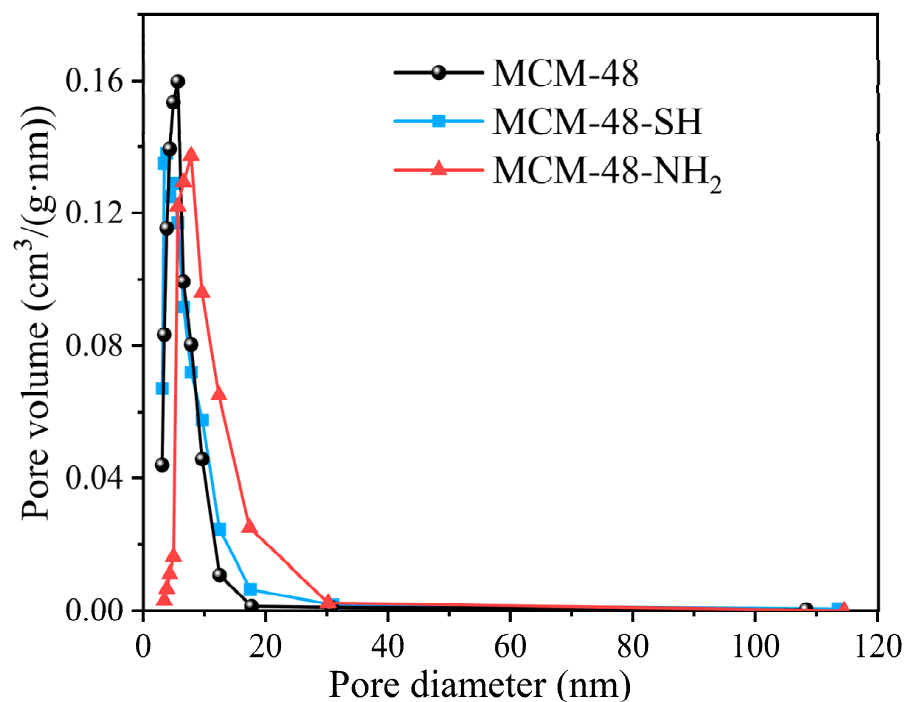


Figure 4. Pore size distribution diagram of MCM-48-SH, MCM-48, and MCM-48-NH₂.

3.1.4. Fourier Transform Infrared Spectroscopy (FTIR) Characterization Analysis

The FTIR spectra of MCM-48, MCM-48-SH, and MCM-48-NH₂ are shown in Figure 5, and each absorption peak in the spectra corresponds to the group vibration [12]. According to the spectral absorption characteristic peak analysis, the characteristic absorption peak of MCM-48 can be clearly observed in the MCM-48-SH band (3414 cm⁻¹, 794 cm⁻¹, and 454 cm⁻¹) [54].

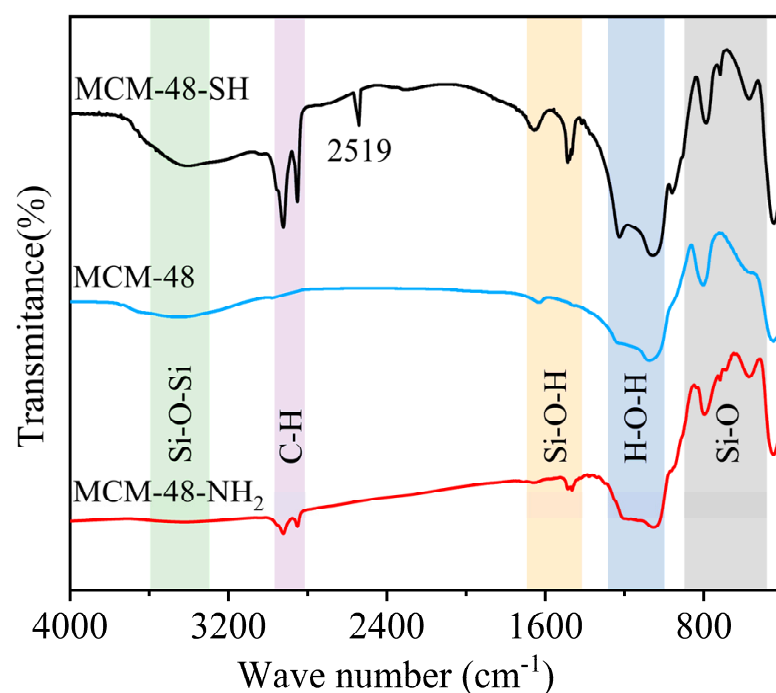


Figure 5. FTIR image of MCM-48-SH, MCM-48, and MCM-48-NH₂.

Compared with the spectrum of MCM-48, MCM-48-SH had three obvious absorption peaks at 2924 cm^{-1} , 2853 cm^{-1} , and 1491 cm^{-1} , and this proved that the characteristic carbon–hydrogen bond of the silane reagent, $-\text{CH}_2-\text{CH}_2-\text{SH}$, was connected to the surface of MCM-48.

The absorption peak of MCM-48-SH at 659 cm^{-1} was sharper than that of MCM-48, which was due to more bound water on the surface of MCM-48-SH. In the MCM-48-SH spectrum, there were many miscellaneous peaks at 794 cm^{-1} , which were due to the slight destruction of the internal structure and a decrease in the order of MCM-48-SH due to the grafting of the sulfhydryl functional group.

The characteristic absorption peak of $-\text{SH}$ was at 2519 cm^{-1} , which proved that the functionalized $-\text{SH}$ group was successfully grafted while retaining the original structure of MCM-48. The absence of a distinct $-\text{NH}_2$ absorption peak at MCM-48- NH_2 was due to the fact that the bond energy of the $\text{C}-\text{C}$ bond was greater than that of the $\text{C}-\text{N}$ bond; therefore, the $-\text{CH}_2-\text{NH}_2$ would prefer a $\text{C}-\text{N}$ bond breaking than a $\text{C}-\text{C}$ bond, resulting in a less distinct absorption peak.

3.2. Adsorption of Cr(VI) by MCM-48-SH

3.2.1. Comparison of the Maximum Adsorption Capacity of Several Mesoporous Materials

Figure 6 shows the effect of MCM-48, MCM-48-SH, and MCM-48- NH_2 after 3 d of adsorption. The three adsorbents showed significantly different removal rates of Cr(VI), with MCM-48-SH being the largest (17.9 mg/g), MCM-48 the second-largest (4.0 mg/g), and MCM-48- NH_2 the smallest (0.5 mg/g).

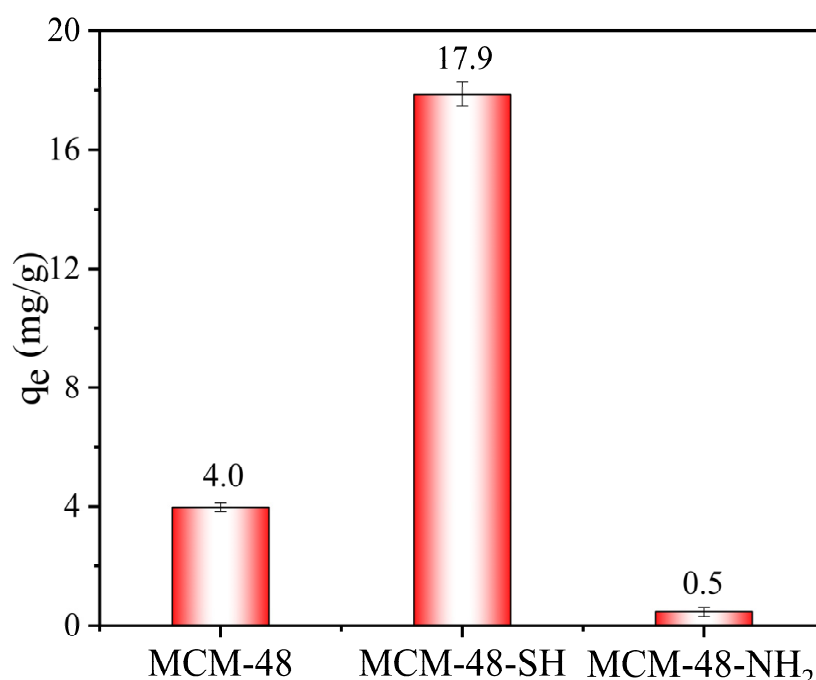


Figure 6. Comparison of the adsorptions of Cr(VI) by MCM-48, MCM-48-SH, and MCM-48- NH_2 (the reaction temperature was $25\text{ }^\circ\text{C}$, the amount of adsorbent was 100 mg , the pH of the solution was 2, and the reaction time was 3 d).

The adsorption comparison of the three adsorbents showed that MCM-48-SH had a better adsorption effect on Cr(VI) than the other two adsorbents and the removal rate was 93.46%. The introduction of $-\text{SH}$ increased the number of functional groups on the outer surface and in the pore channels of MCM-48 and increased the number of adsorption sites, while the introduction of $-\text{NH}_2$ caused the structural collapse of the material. However, $-\text{NH}_2$ had no adsorption effect on Cr(VI), and $-\text{SH}$ played a favorable role in Cr(VI) adsorption, proving the excellent adsorption performance of MCM-48-SH.

3.2.2. Adsorption Isotherm

To investigate the adsorption capacity of MCM-48-SH, the isotherms of Cr(VI) adsorption by MCM-48, MCM-48-SH, and MCM-48-NH₂ at 25 °C were examined (Figure 7). In this study, Langmuir and Freundlich isotherm models were used to study the interaction between adsorbents and Cr(VI). These two gas adsorption models were first applied to microporous adsorbents and then extended to aqueous solute adsorption [55,56]. The Langmuir isotherm model was used for a continuous monolayer adsorption on the surface of homogeneous and flat adsorbents. The Freundlich isotherm model assumes that the heterogeneous surface of adsorbents has multi-layer adsorption [57]. The equations of the Langmuir and Freundlich isotherm models are shown in the Supplementary Materials. According to the fitting data in Table 2, the fitting degree of the Langmuir model of the adsorption isotherm of MCM-48, MCM-48-SH, and MCM-48-NH₂ was greater than that of the Freundlich model. In previous studies [35], the kinetics of heavy metal ion adsorption by MCM-48 modified materials were also primarily predicted using the Langmuir adsorption model.

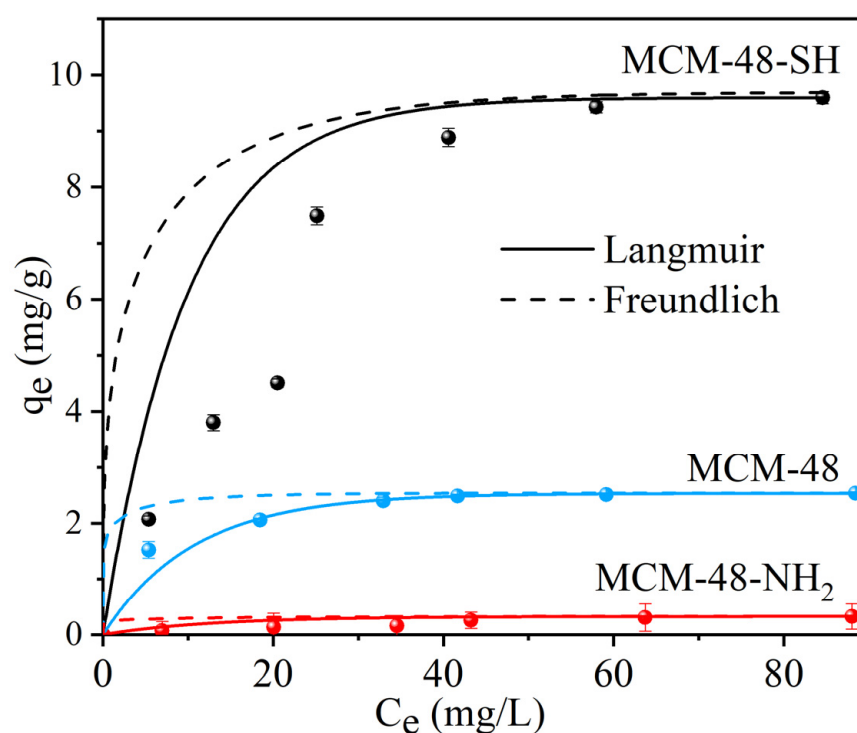


Figure 7. Adsorption isotherm of Cr(VI) adsorption by MCM-48, MCM-48-SH, and MCM-48-NH₂ (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, the pH of the solution was 2, and the reaction time was 3 d).

Table 2. Fitting data of the adsorption isotherm models of MCM-48, MCM-48-SH, and MCM-48-NH₂.

Material	Langmuir			Freundlich		
	$q_{\max}(\text{mg/g})$	K_L	R^2	$1/n$	K_F	R^2
MCM-48	4.13	0.094	0.992	0.108	0.254	0.896
MCM-48-SH	18.3	0.101	0.938	0.067	0.970	0.774
MCM-48-NH ₂	0.506	0.078	0.948	0.094	0.332	0.934

The adsorption isotherm of MCM-48-SH basically agreed with the typical Langmuir adsorption model, and this was consistent with the inference from the N₂ adsorption–desorption curve of MCM-48-SH above [58]. Therefore, the adsorption of Cr(VI) by MCM-48-SH was predicted using the Langmuir model with a maximum adsorption of

18.3 mg/g, which was in agreement with the experimentally measured maximum adsorption of 17.9 mg/g and a maximum removal of 93.45%. The adsorption of Cr(VI) by MCM-48-SH was primarily the result of chemisorption between the -SH group and Cr(VI) and the adsorption of a homogeneous single molecular layer on the material surface and in the pore channels. According to Figure 7, the fitting data of the two adsorption isotherm models of MCM-48-SH were $n > 1$ and $n^{-1} < 0.5$, which indicated that MCM-48-SH had favorable adsorption for Cr(VI).

3.2.3. Adsorption Kinetics

In this study, we applied a pseudo-first-order dynamics model, pseudo-second-order dynamics model, and intraparticle diffusion model to evaluate the adsorption kinetics and the adsorption rate in Figure 8. The pseudo-first-order dynamics model assumes that the reaction rate is only related to the concentration, the pseudo-second-order dynamics model assumes that the adsorption rate is affected by chemical adsorption, and the intraparticle diffusion model mainly explores the diffusion mechanism of the adsorption process. The equations of the models are shown in the Supplementary Materials.

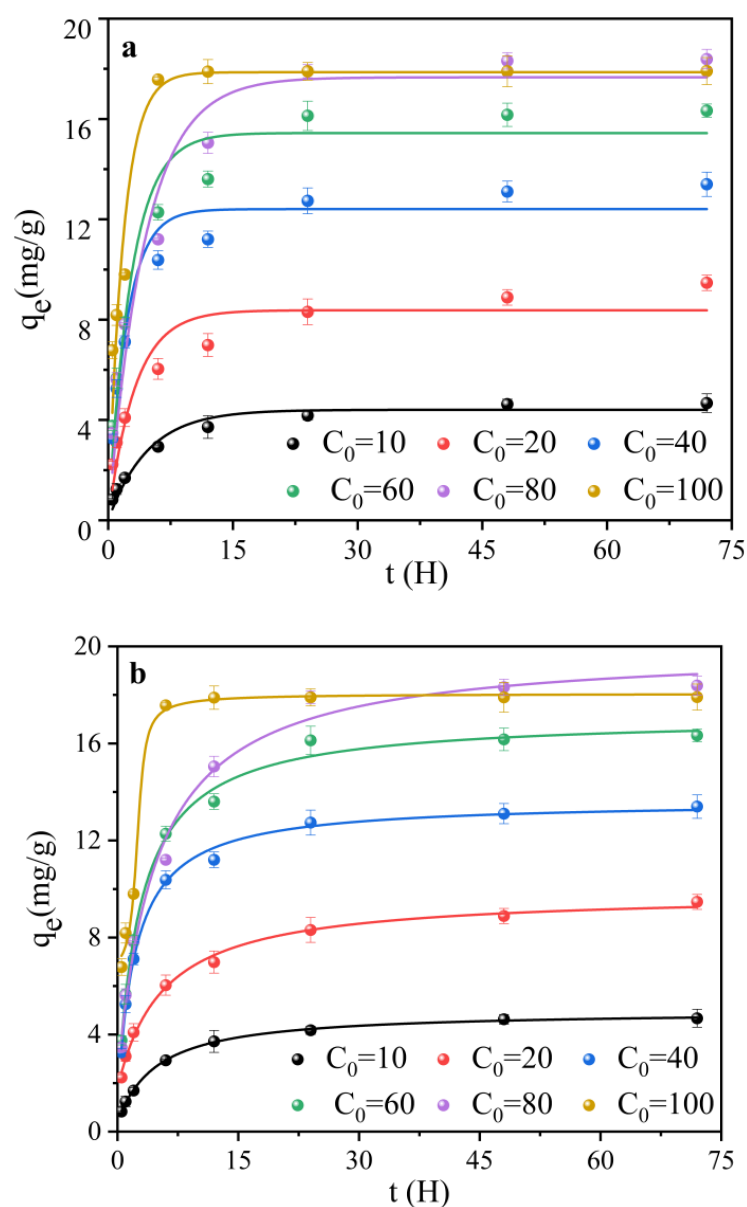


Figure 8. Cont.

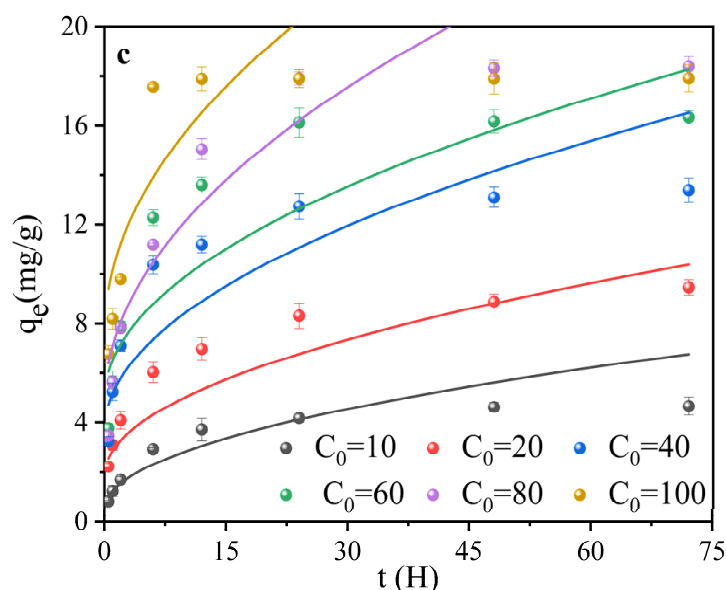


Figure 8. Fitting of the pseudo-first-order adsorption kinetic curve of MCM-48-SH (a); fitting of the pseudo-second-order adsorption kinetic curve of MCM-48-SH (b); fitting of the intraparticle diffusion model of MCM-48-SH (c); (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, the pH of the solution was 2, and the reaction time was 3 d).

According to the data in Table 3, the correlation coefficient (R^2) of the adsorption fitting pseudo-second-order dynamics model was the largest, while the fitting effect of the intraparticle diffusion model was the worst. It did not even fit the adsorption equilibrium. This demonstrated that the adsorption of Cr(VI) by MCM-48-SH was predicted using a pseudo-second-order dynamics model [59–61], where the adsorption rate of Cr(VI) by MCM-48-SH was proportional to the square of the Cr(VI) concentration over a range of concentrations and the adsorption process was mainly controlled by the chemisorption between -SH and Cr(VI).

Table 3. Fitting data of the adsorption kinetics of MCM-48-SH at different concentrations.

C_0 (mg/L)	Pseudo-First-Order Dynamics Model		Pseudo-Second-Order Dynamics Model		Intraparticle Diffusion Model		
	$K_1 (\times 10^{-2})$	R^2	$K_2 (\times 10^{-3})$	R^2	K_p	C	R^2
10	2.11	0.954	1.13	0.973	0.738	0.506	0.847
20	3.11	0.872	1.28	0.929	1.00	1.86	0.923
40	4.53	0.938	4.28	0.966	1.52	3.65	0.747
60	3.59	0.942	3.81	0.969	1.57	4.95	0.758
80	2.27	0.930	1.37	0.957	2.34	4.75	0.818
100	5.49	0.927	2.24	0.963	2.58	7.58	0.414

During the process of adsorption, the adsorption rate at the initial stage was very fast and then it gradually slowed down until the adsorption equilibrium was reached in approximately 24 h. The fast adsorption rate at the beginning of the reaction was primarily due to the ordered mesoporous structure of MCM-48-SH and the -SH in the pore channels that allowed the rapid adsorption of Cr(VI) on the surface of MCM-48-SH and in the pore channels. With the adsorption sites of -SH gradually occupied by Cr(VI), the adsorption rate of Cr(VI) by MCM-48-SH slowed down. According to the experimental results, the adsorption rate was positively correlated with the solution concentration until the maximum adsorption equilibrium amount (80 mg/L) was reached, after which it gradually stabilized.

With the increase in initial solution concentrations, the adsorption capacity of MCM-48-SH for Cr(VI) increased until it reached 80 mg/L. The removal rate of MCM-48-SH at 80 mg/L was almost the same as that at 10 mg/L. When the concentration of Cr(VI) in the solution was 100 mg/L, the adsorption capacity no longer increased with the increase in concentrations because Cr(VI) occupied the active adsorption sites, and the removal rate of Cr(VI) decreased with the increase in concentration. The results showed that the initial concentration of Cr(VI) affected the adsorption rate of MCM-48-SH but had little effect on the final removal rate, which was consistent with the results shown in other studies [62,63].

3.2.4. Influence of the pH Value on the Adsorption Effect

The pH value is important to the adsorption of Cr(VI) [64–67]. The pH value affects the charge and chemical characteristics of the adsorbent MCM-48-SH surface. The point of charge (PZC) value of MCM-48-SH was 4.8.

According to Figure 9, when the solution was alkaline, the main existing form of Cr(VI) was CrO_4^{2-} and the adsorption was not obvious; therefore, we mainly studied the adsorption of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- in the aqueous solution when the pH value was 2–6. When the initial pH value of the solution was 6 (>4.8), the surface of MCM-48-SH was negatively charged and attracted cations; therefore, the adsorption effect of MCM-48-SH was greatly reduced. When the initial pH value of the solution was less than the PZC value of MCM-48-SH, the surface of MCM-48-SH was positively charged and attracted anions, thereby promoting adsorption. The main existing form of Cr(VI) was $\text{Cr}_2\text{O}_7^{2-}$, and MCM-48-SH had the best adsorption effect on $\text{Cr}_2\text{O}_7^{2-}$ when the pH value was 2.

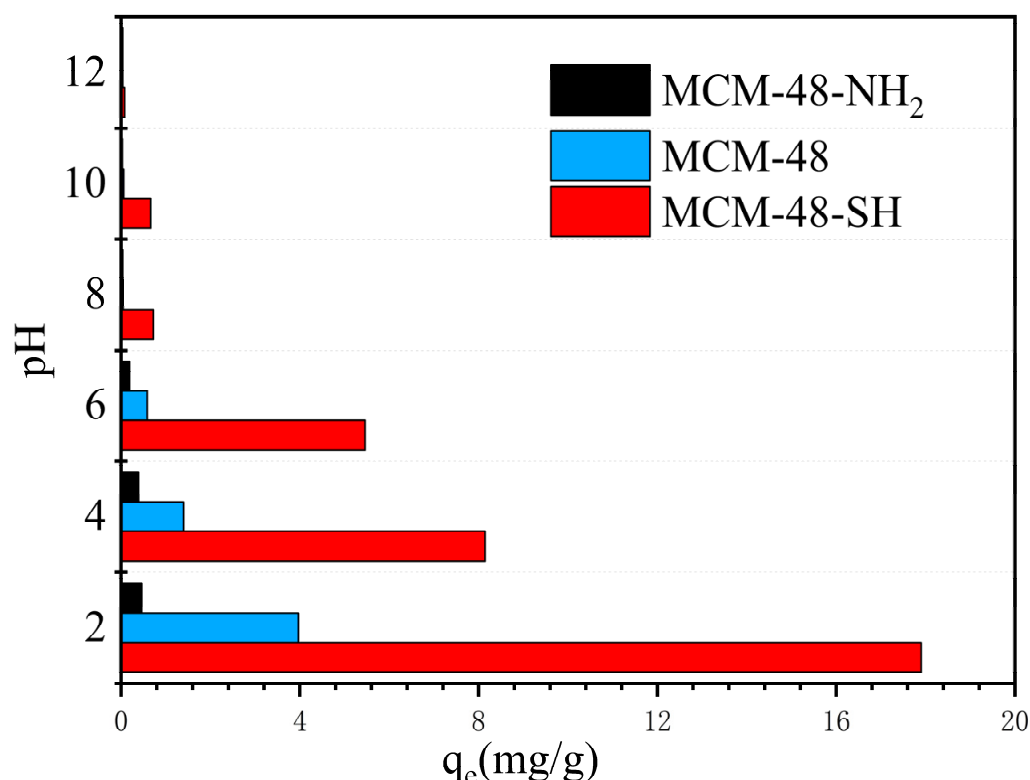


Figure 9. Adsorption effect diagram of MCM-48-SH, MCM-48, and MCM-48-NH₂ at different pHs (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, and the reaction time was 3 d).

The adsorption of Cr(VI) by MCM-48-SH was $\text{Cr}_2\text{O}_7^{2-}$ dominated, and when the solution environment was acidic, $\text{Cr}_2\text{O}_7^{2-}$ was the primary form present. Hence, the adsorption effect was good. When the solution environment was neutral and basic, CrO_4^{2-} was the primary form present and the surface of MCM-48-SH also changed from a positive

to a negative charge; in addition, the adsorption effect on Cr(VI) was greatly reduced. Similar results were found in other scholars' studies on the effect of pH on the adsorption of Cr(VI) [68–71].

3.2.5. Influence of the Coexisting Ions in the Wastewater on the Adsorption Effect

Figure 10 demonstrates the effect of Cr(VI) adsorption by MCM-48-SH under different coexisting ion solution environments. The effect of four common metal ions (Cu^{2+} , Fe^{3+} , Pb^{2+} , and Zn^{2+}) on the adsorption of Cr(VI) by MCM-48-SH was small and almost negligible. This is because MCM-48-SH has no adsorption effect on metal cations, the addition of metal cations neutralizes the charge repulsion between MCM-48-SH and $\text{Cr}_2\text{O}_7^{2-}$, and the existing balance of Cr(VI) in the solution moves to (1). In addition, metal cations can replace the H in $-\text{OH}$ and $-\text{SH}$ on the surface of MCM-48-SH and inhibit the formation of hydrogen bonds and this can also lead to a reduction in the adsorption capacity.

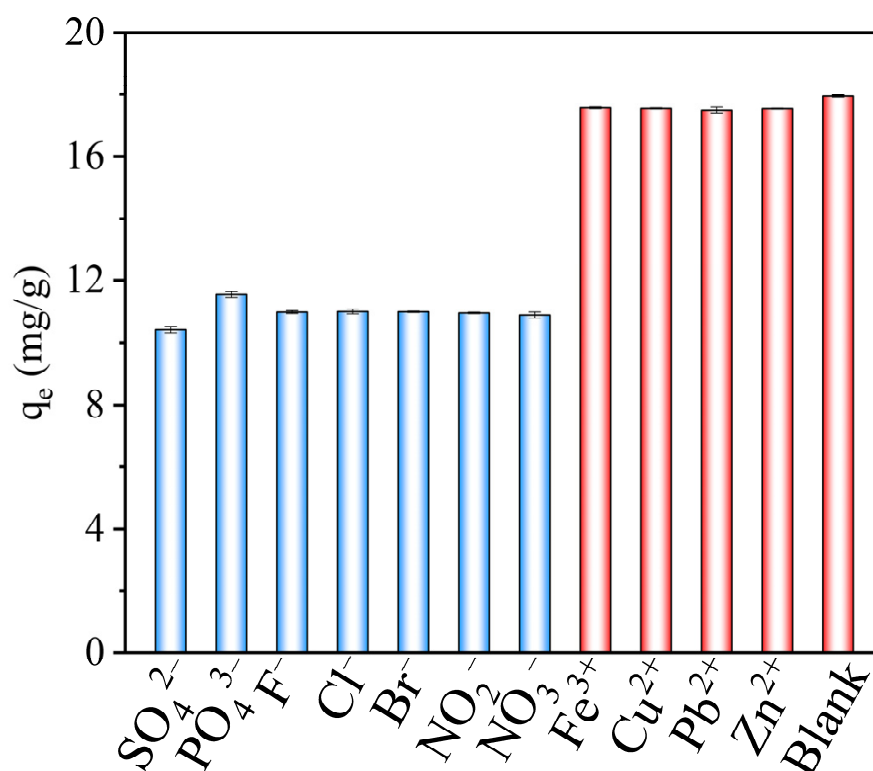
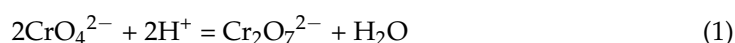


Figure 10. Adsorption of Cr(VI) by MCM-48-SH under different coexisting ionic conditions (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, the pH of the solution was 2, and the reaction time was 3 d).

The coexisting anions (F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}) in the aqueous solution had an obvious influence on the adsorption of Cr(VI). These can be divided into the following categories: univalent anion, bivalent anion, and multivalent anion; among these, Cl^- , PO_4^{3-} , and SO_4^{2-} were the most obvious, as shown in Figure 11. The adsorption of Cr(VI) on MCM-48-SH will be reduced by different anions. The adsorption of Cr(VI) by MCM-48-SH decreased as the concentration of co-existing anions increased, and the significant effect of the ionic strength on the adsorption further illustrated that the adsorption process was influenced by the electrostatic attraction between MCM-48-SH and Cr(VI). The effect of each anion on adsorption varied at the same ion concentration, SO_4^{2-} had the greatest influence on the adsorption effect, Cl^- was second, and PO_4^{3-} had the smallest influence on the adsorption effect.

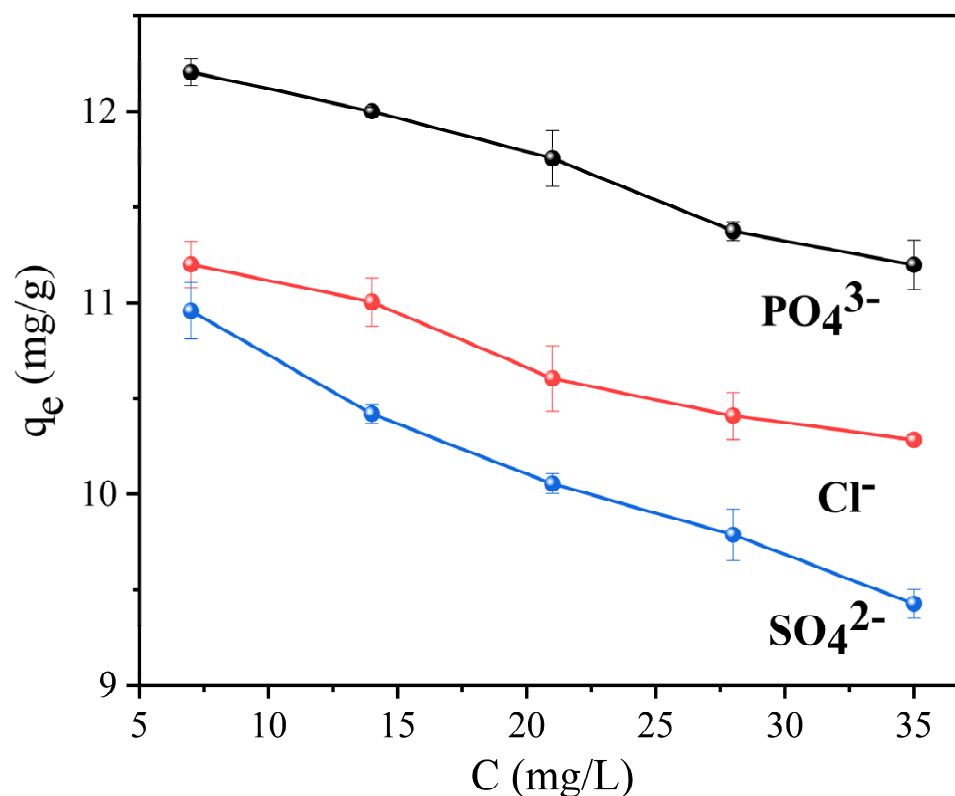


Figure 11. Adsorption effect diagram of MCM-48-SH under the three different coexisting ions in solution (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, the pH of the solution was 2, and the reaction time was 3 d).

When other anions coexist in the solution, they will compete for the adsorption sites [72,73] and this will affect the adsorption effect of MCM-48-SH. With the increase in anion concentration, anions occupied the adsorption site of MCM-48-SH, which led to a decrease in Cr(VI) adsorption capacity [61]. Owing to the different adsorption competitiveness of the different anions, SO_4^{2-} had the greatest influence, followed by Cl^- , and PO_4^{3-} . SO_4^{2-} is a multivalent anion with a similar structure and size to $\text{Cr}_2\text{O}_7^{2-}$. Therefore, compared with the amount of Cl^- and PO_4^{3-} , it had strong adsorption competitiveness.

3.2.6. Adsorption Comparison between the Traditional Adsorbent and MCM-48-SH

Compared with other types of adsorbents, the pH value of the solution that affects the adsorption of Cr(VI) by CAC and BTT was first explored [46,47]. As shown in Figure 12, when the pH = 4, the adsorption effect of CAC was the best. When the pH was 6, the BTT adsorption effect was the best.

Under the above adsorption conditions, the adsorption effects of CAC, BTT, and MCM-48-SH on Cr(VI) were compared, as shown in Figure 12. According to the image, MCM-48-SH had the largest adsorption capacity for Cr(VI), followed by CAC, and BTT had the smallest adsorption capacity for Cr(VI). This is due to the fact that the adsorption of Cr(VI) by MCM-48-SH was primarily due to the more toxic $\text{Cr}_2\text{O}_7^{2-}$, which was the primary form of Cr(VI) present at pH 2–3, whereas the adsorption of Cr(VI) by CAC and BTT was primarily physical and was not greatly affected by pH.

By combining the characterization data with the adsorption experimental results, it can be seen that compared with the microstructure of CAC and BTT, the unique spherical mesoporous structure of MCM-48-SH was more conducive to the adsorption of Cr(VI). In addition, combined with the FTIR data, MCM-48-SH not only had the typical mesoporous structure characteristics but also had grafted sulfhydryl groups that modified the surface of the mesoporous structure and enhanced its adsorption capacity for Cr(VI).

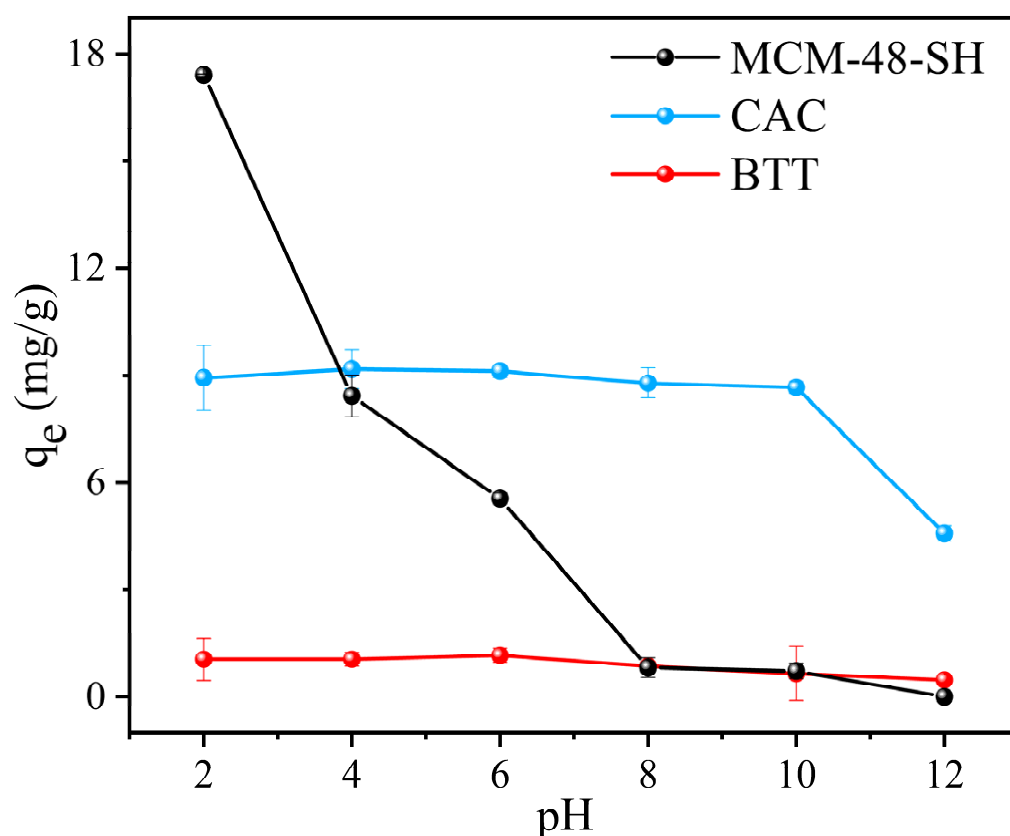


Figure 12. Adsorption effect diagram of the three adsorbents at different solution pHs (the reaction temperature was 25 °C, the amount of adsorbent was 25 mg, and the reaction time was 3 d).

4. Conclusion

The conclusions of this study are as follows:

- (1) A modified mesoporous nanomaterial (MCM-48-SH) was prepared in this experiment. Through a series of characterization analyses, such as SEM, BET, XRD, and FTIR, it was found that MCM-48-SH was a standard mesoporous material with an average diameter of 2.5 μm and an average pore diameter of 4 nm. The introduction of -SH groups reduced the ordering of the materials;
- (2) The optimal adsorption concentration of MCM-48-SH for Cr(VI) was 80 mg/L and the optimum pH value was 2. The metal cations in the solution had little effect on adsorption, while the anions did reduce the adsorption capacity, among which SO_4^{2-} had the most obvious influence;
- (3) The adsorption of Cr(VI) by MCM-48-SH accorded with the Langmuir isothermal adsorption model and pseudo-second-order dynamic model. Experimental data showed that the maximum adsorption capacity reached 17.9 mg/g and the removal rate reached 93.45%. MCM-48-SH showed a typical mesoporous structure, grafted sulfhydryl groups, and good dispersibility in water, which caused it to have good adsorption properties. It was shown to be a high-efficiency adsorbent for removing Cr(VI) from wastewater;
- (4) Compared to CAC and BTT, MCM-48-SH showed better adsorption of $\text{Cr}_2\text{O}_7^{2-}$. Therefore, MCM-48-SH showed better adsorption of Cr(VI) at $\text{pH} < 4$ and CAC showed better adsorption of Cr(VI) at $\text{pH} > 4$. In subsequent studies, it is hoped that more efficient adsorption of Cr(VI) can be achieved by optimizing the adsorbent material or adjusting the pH of the agent.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15030524/s1>. Figure S1. Experimental appliance. Figure S2. Preparation diagram of MCM-48-SH. Figure S3. SEM image MCM-48-SH; MAM-48-SH-S1; MAM-48-SH-S2; MAM-48-SH-S3. Figure S4. SEM image MCM-48-NH₂. Figure S5. Adsorption kinetics curve of MCM-48 and MCM-48-NH₂. Figure S6. Adsorption of MCM-48 (left) and MCM-48-NH₂ (right) under the influence of co-existing ions. Table S1. Each absorption peak of the FTIR spectrum corresponded to the group vibration. Refs. [13,48,49,74–77] have been cited in the supplementary materials.

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