Ultra-efficient copper ions adsorption of Chitosan-montmorillonite composite aerogel for wastewater treatment

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Abstract
The modified montmorillonite(MMT) has a two-dimensional stable and ordered lamellar structure. The addition of chitosan(CS) cross-links the two-dimensional sheets to build a three-dimensional network structure with a high specific surface area. We have prepared the best MMT-based water treatment materials that have been reported. This new type of aerogel can efficiently absorb heavy metal ions in wastewater. The structure and performance of the composite material were characterized in this article. Besides, the adsorption kinetics, adsorption thermodynamics, pH influence, and recycling performance are all focused on. The adsorption equilibrium time of CS-MMT2 is 50 min. The removal rate of Cu\textsuperscript{2+} is as high as 98.21\%. The maximum adsorption capacity is 86.95 mg/g. The adsorption process of Cu\textsuperscript{2+} by CS-MMT composite aerogel conforms to the
quasi-second-order kinetic model and the Langrangian adsorption isotherm. After three cycles, the removal rate of Cu$^{2+}$ by CS-MMT2 remained above 80%. This article also involves the discussion of the material's adsorption mechanism for Cu$^{2+}$. This is a kind of environmentally friendly material that can be mass-produced, cheap, efficient, and excellent, which is of great significance to the development of environmental protection.

**Key Words:** Chitosan, Montmorillonite, Cu$^{2+}$, Aerogel, Environmental protection

0. Introduction

With the exploitation of natural resources, the pollution of water resources has attracted much attention (Kolpin et al. 2002). In several countries and regions, it has already exceeded the self-purification capacity of natural water bodies, causing much severe environmental pollution (Fu and Wang 2011). Heavy metal pollution is one of the most important parts of the water environment pollution (Jarup 2003; Zou et al. 2016). In industry and agriculture, a large number of pollutants, including heavy metals, have been discharged into rivers, which resulted in deteriorating water quality, causing a series of serious consequences (Bailey et al. 1999).

Copper is an essential trace element in the human body. It can be absorbed from various sources, such as food, dust, and water. Excess copper may lead to several symptoms such as nausea, vomiting, abdominal muscle pain. Accumulating in the liver, it may cause various diseases such as gastrointestinal discomfort, kidney, and liver damage (Thit et al. 2020). It can be fatal at extreme doses (Shabbir et al. 2020). Therefore, it is essential to remove residual copper ions in water. Numerous articles have reported various sewage treatment methods containing heavy metal ions, including adsorption, ion exchange, chemical precipitation, membrane filtration, electrochemical
techniques, and reverse osmosis (Moja et al. 2020). Compared with others, adsorption is a simple, easy-to-operate, and inexpensive way to treat heavy metal ions (El-Kousy et al. 2020). Recent research has focused on relatively low-cost adsorbents such as zeolite (Bailey et al. 1999), montmorillonite (Uddin 2017), kaolinite clay (Yuan et al. 2015), mineral silicate (Luo et al. 2010), sepiolite (Sun et al. 2013), chitosan polymer (Wan et al. 2010), and biological packing (Wu et al. 2004), etc. For any adsorbent, the adsorption capacity is the most critical technical indicator. Especially for low-concentration heavy metal ion wastewater, the development of nano-adsorption materials has a long way to go (Liu et al. 2020b). Therefore, it is necessary to obtain a new adsorbent with high adsorption capacity, high specific surface area, rich pore structure, abundant sources, low cost, good stability, easy recovery, and regeneration.

In recent years, aerogel has been considered a promising insulation material. (Baetens et al. 2011) At the same time, high porosity and large specific surface area show superior adsorption capacity (Cui et al. 2018). It can be widely used in sewage treatment, air purification, nuclear waste treatment, and other environmental protection fields (Pierre and Pajonk 2002).

Modified clay, such as montmorillonite, is regarded as one of the best inorganic adsorbents because of its high utilization rate, friendly environment, and high negative charge, which can absorb positively charged metal ions (Mahouachi et al. 2020). Chitosan is hydrophilic, biocompatible, biodegradable, non-toxic, has high mechanical strength and film-forming properties, as well as antibacterial properties (Li et al. 2016). The amino (-NH₂) and hydroxyl (-OH) groups inherent in the chemical structure of chitosan are the main functional groups that adsorb various heavy metals in water. By modifying the structure of chitosan with -COOH group, its solubility at pH=7 can be increased without affecting the above properties (Wang et al. 2017). Studies have
shown that ionic imprinted montmorillonite nanosheet/chitosan (IIMNC) gel beads provide active adsorption sites through their highly efficient cation exchange performance for the selective adsorption of Cu\(^{2+}\) (Qin et al. 2020). The montmorillonite-chitosan composite material can provide hydrophobicity and functional groups to improve the performance of montmorillonite in wastewater treatment (Hu et al. 2017b). The interaction sequence of adsorption-related groups in the chitosan-Montmorillonite composite showed that the adsorption capacity of bonding with NH\(_3^+\) may be greater than that of bonding with hydroxyl (Hu et al. 2017a). The clay-chitosan nanocomposite material is expected to achieve a major breakthrough in the treatment of heavy metal ion wastewater.

Our team combined chitosan aerogel and montmorillonite designed a new high-efficiency adsorbent. Montmorillonite can be used as ideal templates for preparing nanomaterials and supporting chitosan hydrogels due to their high surface area and stable structure. We use the LiOH/urea dissolving system to process chitosan raw materials and the chemical precipitation method to compound Montmorillonite. By adjusting the concentration of the initial reactants, the size, pore size, and mechanical properties of the synthesized CS-MMT aerogel can be determined. CS-MMT aerogel nanocomposite can be used as an environmentally friendly adsorbent for the removal of Cu\(^{2+}\) from wastewater. With its outstanding performance, it will occupy a place in the field of wastewater treatment. The adsorption kinetics and adsorption thermodynamics were used to systematically study the maximum adsorption capacity. The separation and reusability of CS-MMT aerogel were also studied in detail.

1. Experimental Section

1.1 Fabrication of CS-MMT aerogel

CS-MMT aerogel was prepared by sol-gel method (SI Fig. 1), which could be broken and
regenerated at low temperature (SI Section 1). According to the absorbance value of Cu$^{2+}$ in the supernatant, the concentration, adsorption capacity, and removal efficiency of Cu$^{2+}$ in the remaining solution were calculated using equations ((1)-(4)).

\[ A = 0.0191C + 0.0124 \]  
\[ Ce = \frac{C}{V_1} \]  
\[ Qe = \frac{(C_0 - C_e) \times V_2}{m_1} \]  
\[ S(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \]

Where \( C \) is the content of Cu$^{2+}$ in the residual solution after adsorption, which can be calculated by different absorbance values(\( \mu g \)). \( C_0 \) before for adsorption of Cu$^{2+}$ solution concentration (mg/mL). \( C_e \) for the adsorption of Cu$^{2+}$ solution concentration (mg/mL). \( m \) is obtained from the standard curve of Cu$^{2+}$ dosage (\( \mu g \)). \( m_1 \) as adsorbent dose (mg). \( V_1 \) for copper water volume (mL). \( Qe \) for equilibrium adsorption Cu (II) the amount of (mg/g). \( V_2 \) to join Cu$^{2+}$ the volume of a solution (mL), \( S \) for Cu$^{2+}$ removal efficiency.

2. Results and discussion

2.1 XPS, XRD and FT-IR analysis
Fig. 1 (a) XPS survey spectrum, (b–f) C1s spin-orbit peaks of CS-MMTs, (g) XRD patterns of CS-MMTs and MMT, (h) FTIR spectra of CS-MMTs

To further analyze the interaction between MMT and CS matrix, X-ray photoelectron spectroscopy is used to analyze the surface chemical state of different components of CS-MMTs (Fig. 1(b–f)). The C spectrum shows that the CS-MMTs are rich in C-C, C=O, and C-O/C-N groups. The peak at 283.9 eV corresponds to the binding energy of the C-N bond, and the peaks of C=O and C-C mainly appear at about 286.8 eV and 285.0 eV. (Wu et al. 2020). Compared with other components, the C1s of CS-MMT2 is significantly enhanced, and the intensity of the C-N peak is also significantly increased, proving that MMT was successfully modified by CS. The O1s (531.8 eV) peak is attributed to hydroxyl oxygen, indicating that siloxane was successfully converted to hydroxyl oxygen. (Guo et al. 2019). However, the N-element XPS spectrum showed a certain
amount of C-N and N-O in CS-MMT. Besides, peaks of Si 2p(103eV) and Mg2p (55eV) corresponding to MMT were found in the spectrum of CS-MMT2 (Akar et al. 2020), indicating the successful combination of CS and MMT.

The crystal phase and phase composition of CS-MMT composite aerogel were analyzed by XRD (Fig. 1 (g)). According to extensive studies, MMT is a clay mineral in the form of octahedral crystals. The characteristic spikes show high crystallinity of nano-MMT at 5.9°, 19°, and 26°. According to the Scherer equation, we can easily calculate that the interlayer spacing of nano-montmorillonite is 1.593nm. In contrast, the XRD patterns of the chitosan-modified montmorillonite composite aerogels have obvious changes, indicating that the crystal structure of the composite aerogel has changed significantly. By comparing and analyzing the standard spectra, we can infer that the crystal structure of CS-MMT is roughly the same as that of square quartz. Besides, we can notice that there is a broad peak at 29°. As the ratio of nano-montmorillonite increases, the peak intensity gradually decreases. We attribute this to the cation exchange between the protonated amino groups of chitosan and the cations in the montmorillonite layer, which results in such formation of disordered exfoliation structures.

As shown in Fig.1(h), the hydroxyl groups of amide or hydroxide combined with amino groups in montmorillonite and chitosan mainly appear at about 3400 cm⁻¹, which is consistent with previous reports (Liu et al. 2020a). The amide stretching of the chitosan-modified montmorillonite composite appeared at about 1640 cm⁻¹. All the CS-MMT composite aerogels showed characteristic silica sharp bands around 1031 cm⁻¹. The bending vibrations of Si-O-Mg and Si-O-Si appeared at 1527 cm⁻¹ and 470 cm⁻¹, respectively (Zhu et al. 2017). There are strong peaks at 3440 cm⁻¹ and 1659 cm⁻¹, which correspond to the overlapping stretching vibrations of hydroxyl and amino groups and the stretching
vibrations of carboxyl groups. The peak at 1332 cm\(^{-1}\) is the stretching vibration of amino. The FT-IR is a great proof of the successful preparation of CS-MMT composite aerogels.

### 2.2 SEM analysis

![SEM images](image)

**Fig. 2** SEM image of (a)CS-MMT1, (b)CS-MMT2, (c)CS-MMT3, (d)CS-MMT4, (e)CS-MMT5

As is shown in Fig. 2, the CS-MMT composite aerogels of different components all present a clear layered structure. CS connects the montmorillonite laminates in a fiber-like cross-linking manner. As shown in Fig. 2(b), CS-MMT2 composite aerogel has a large number of thin-layer structures and a certain interlayer space. The doping of CS cross-links the layers of MMT to build a micron-level pore structure. This three-dimensional porous structure can greatly increase the specific surface area of the material, laying a solid foundation for the adsorption of heavy metal ions. The C, N, O, and Si elements of CS-MMT2 aerogel are uniformly distributed. It contains a large number of oxygen-containing functional groups, oxides, and nitrides. By TG analysis, CS-MMT showed higher degradation temperature (SI Section 2, Fig. S2, and S3).

### 2.2 The Specific surface area and pore size analysis
Fig. 3 (a) Mercury intrusion test, (b–f) N\textsubscript{2} Adsorption–desorption isotherms and pore size distributions of CS-MMT composite aerogels with different components

The shape of this type of hole should be a slit-like tubular capillary structure with both ends open. (Zhao et al. 2020). As is shown in Fig.3(a–f), when the relative pressure P/P\textsubscript{0} was 0-0.6, the N\textsubscript{2} adsorption increased slowly, which proved that there were a few micropores in the samples. In this stage, nitrogen molecules are gradually adsorbed from monolayer to multilayer into the porous structure. Subsequently, when the relative pressure was between 0.6-0.99, the nitrogen adsorption capacity at the high-pressure end increased sharply, indicating the presence of mesopore and macropore in the material. According to the physical property parameters in SI Table S1, the specific surface area of CS-MMT2 is relatively high, which is 14.133m\textsuperscript{2}/g, and the pore diameter distribution was uniform. Combined with SEM images(Fig.1(b)), it was found that there was a stable three-dimensional network structure. (Chu et al. 2019). Because the nitrogen adsorption and desorption specific surface and pore size test can be widely used in the test of porous materials with mesoporous structure, it is only of reference value for macroporous materials. We conducted mercury intru
tests on all five CS-MMT samples. According to the analysis of mercury injection pore size, the pores are mainly mesopore and macropore. The average pore sizes of composite aerogels are 1242.89 nm (CS-MMT1), 889.29 nm (CS-MMT2), 1012.60 nm (CS-MMT3), 3942.97 nm (CS-MMT4), and 1159.19 nm (CS-MMT5). The pore size ranges from 50-100 μm. Undoubtedly, large specific surface area and porous structure provided more abundant active sites for rapid absorption of Cu²⁺.

2.3 Structure model and adsorption mechanism

![Fig. 4 Schematic diagram of structure model and adsorption mechanism](image)

According to detailed characterization data, we can get the following material structure model (Fig. 4). The montmorillonite layer is modified by organic quaternary ammonium salt ions. Combined with the XRD diffraction pattern, it can be seen that the interlayer spacing of montmorillonite increases from 1.236 to 1.593 nm. XRD, FT-IR, and XPS are used for detailed elements and surface state analysis. We speculate that strong alkali treatment and ball milling break the Si-O and Mg-O bonds of the unit cell in montmorillonite. The amino groups of chitosan cross-link the active bonds and the -OH and amino groups carried by the surface sheet, forming such CS-
MMT composite aerogel. Cu$^{2+}$ will not only chelate and react with the broken bonds on the surface of CS-MMT, at the same time, the pores and lamella structure of the aerogel are also positively related to the adsorption capacity.

2.4 Adsorption property of CS-MMTs towards Cu$^{2+}$

Adsorption equilibrium time and adsorption kinetics

CS-MMT composite aerogel adsorbed Cu$^{2+}$ at different times (SI Section 2). The adsorption rates of the five adsorbents at different times are sorted in Fig. 5. It can be seen from the adsorption curve and adsorption efficiency that all adsorbents have a high adsorption efficiency of Cu$^{2+}$ in the initial stage of the adsorption reaction. As time goes on, the adsorption process slows down until an adsorption equilibrium is finally reached. In the initial stage of adsorption in this experiment, the Cu$^{2+}$ adsorption material causes concentration diffusion in the solution, and the active adsorption sites on the montmorillonite can combine with Cu$^{2+}$ at different adsorption rates and numbers. As the concentration gradient of Cu$^{2+}$ decreases, the adsorption behavior on the adsorbent gradually decreases, which in turn causes the adsorption rate to slow down. At the same time, as the chelation reaction progresses, the adsorption sites are gradually occupied, and the adsorption reaction reaches equilibrium. From the relationship between adsorption time and adsorption efficiency, it can be seen that the adsorption efficiency of different components of CS-MMT composite aerogel on Cu$^{2+}$ is not significantly different under the same experimental conditions. The adsorption efficiency of CS-MMT2 can be around 99%, and the adsorption equilibrium was reached at about 50min, indicating that CS-MMT2 composite aerogel has a strong adsorption capacity for Cu$^{2+}$. To elucidate the adsorption kinetics of CS-MMT composite aerogel on Cu$^{2+}$, the quasi-first-order model (Eq5) and quasi-second-order model (Eq6) were used to fit the adsorption data of Cu$^{2+}$ as follows:
\[ \lg(Q_e - Q_t) = \lg Q_e - \frac{k_1 t}{2.303} \quad (5) \]

\[ \frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e} \quad (6) \]

Where \( Q_e \) is the adsorption amount when the adsorption process reaches adsorption equilibrium (mg/g), \( Q_t \) is the adsorption amount corresponding to \( t \) at a certain moment in the adsorption process (mg/g), \( k_1 \) and \( k_2 \) are pseudo-first-order (min\(^{-1}\)) and pseudo-second-order rate constants (g/(mg·min\(^{-1}\))), respectively.

**Fig. 5** Adsorption efficiency of CS-MMT composite aerogels for Cu\(^{2+}\) at different time

The parameters of the two models are shown in SI Table S2. By comparing the correlation coefficient R\(^2\) of the two models, it is obvious that the pseudo-second-order kinetic equation has a good correlation with the adsorption process. This indicates that the adsorption rate is more related to the number of unoccupied active sites. As the layered space of montmorillonite increases, the porosity increases. This will directly increase the number of active sites and increase the adsorption capacity.
of Cu$^{2+}$. Based on the quasi-second-order kinetic equation model, the quasi-second-order rate equation of CS-MMT was shown in Fig. 6. According to the fitting curve of CS-MMTs, the corresponding correlation coefficient $R^2$ was calculated. The $R^2$ of CS-MMTs indicates that the adsorption of Cu$^{2+}$ in this system follows a pseudo-second-order kinetic model. CS-MMT2 has the best fit, which can reach 0.99937, while $Q_e$ is 9.906 and $K_2$ is 0.04942.

![Fig. 6 Pseudo-second-order model for adsorption of Cu$^{2+}$ on CS-MMT composite aerogels](image)

**Adsorption isotherms and adsorption thermodynamics**

As can be seen from Fig. 7, the equilibrium adsorption capacity of the three adsorbents to copper ions increased with the increase of the initial concentration of Cu$^{2+}$ solution until the adsorption was completed. When Cu$^{2+}$ solution is at a low concentration, the adsorption curve rises very fast. When the initial concentration increases to a certain concentration, the increasing rate of adsorbent adsorption gradually slows down, and the curve flattens out to near saturation adsorption.
In order to obtain the thermodynamic mechanism of adsorption of Cu\(^{2+}\) by CS-MMT composite aerogels at different initial concentrations, the Langmuir equation and Freundlich equation were used to fit the experimental data. The Langmuir isotherm model (Eq. 7) and the Freundlich isotherm model (Eq. 8) are as follows:

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (7)
\]

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)
\]

Where \(Q_e\) is the adsorption amount of Cu\(^{2+}\) per unit mass of adsorbent at the adsorption equilibrium (mg/g), \(Q_m\) represents the maximum adsorption capacity of Cu\(^{2+}\) (mg/g), and \(C_e\) represents the equilibrium concentration of Cu\(^{2+}\) after adsorption (mg/L), where \(K_L\) and \(K_F\) are the adsorption equilibrium constants of Langmuir isotherm equation and Freundlich isotherm equation, and \(1/n\) is the heterogeneity factor.

As can be clearly seen in Fig.10, the equilibrium adsorption capacity of the five adsorbents on Cu\(^{2+}\) showed a different increasing trend with the increase of the initial concentration of Cu\(^{2+}\) solution. When Cu\(^{2+}\) is at a low concentration, the adsorption curve rises very fast. When the initial concentration increases to a certain concentration, the increasing rate of adsorbent adsorption volume gradually slows down, and the curve flattens out until it approaches saturation adsorption.
Fig. 7 Adsorption capacity of CS-MMT composite aerogels for Cu$^{2+}$ in different initial solution concentration.

The adsorption data were correspondingly fitted to the Langmuir model. The fitting equations of CS-MMTs are shown in Fig. 8. The Langmuir and Freundlich parameters for adsorption of Cu$^{2+}$ are sort in SI Table S3, respectively. The maximum adsorption capacity of the CS-MMTs on Cu$^{2+}$ can be estimated according to the Langmuir adsorption model. Under the optimal conditions, the maximum adsorption capacities of CS-MMT composite aerogels for Cu$^{2+}$ were estimated to be 80.38 mg/g, 86.95 mg/g, 76.92 mg/g, 69.93 mg/g, and 60.86 mg/g, respectively. Compared with the montmorillonite adsorbent reported in the literature, the CS-MMT2 composite aerogel prepared by this experiment showed quite outstanding adsorption capacity for Cu$^{2+}$ (Table 1). The digital image of the adsorption effect is shown in SI Fig. 4. With the addition of the adsorbent for about 30s, the blue complex will initially form until it becomes stable. After adsorption and centrifugation, the solution was obviously
close to the colorless state.

Fig. 8 Langmuir isotherms plots of Cu$^{2+}$ adsorption on CS-MMTs

Table 1 Comparison with other published work

| Researchers | Adsorbent      | Cu$^{2+}$ Adsorption | Ref.          |
|-------------|----------------|----------------------|---------------|
| Chen et al. | Fe$_3$O$_4$-CS/EDTA | 36.52 mg/g        | (Chen et al. 2019) |
| Chu et al.  | Arg-Mt          | 29.15 mg/g          | (Chu et al. 2019) |
| Study          | Modification                  | Capacity (mg/g) | Reference                |
|----------------|-------------------------------|-----------------|--------------------------|
| Chu et al.     | Histidone modifies montmorillonite | 30.72           | (Chu et al. 2020)        |
| Chu et al.     | Montmorillonite was modified by diamino surfactant-containing tetra ammonium cation | 29.03           | (Chu et al. 2020)        |
| Zhang et al.   | Magnetic bentonite/carboxymethyl chitosan/sodium alginate hydrogel sphere | 56.79           | (Zhang et al. 2019)      |
| Wu et al.      | Magnetic polysaccharide/Go @Fe₃O₄ gel beads | 55.96           | (Wu et al. 2019)         |
| This work      | CS-MMT                        | 86.95           |                          |

2.5 The influence of pH on the adsorption effect
It can be seen from Fig. 9 that the Cu$^{2+}$ adsorption capacity of CS-MMT2 increases first and then decreases with the increase of the pH of the solution. When the solution is in a low pH range (3.0~4.0), the adsorption effect of CS-MMT2 is limited. This phenomenon can be interpreted as the presence of excess hydrogen ions under a low pH condition, which limits the reaction of chitosan and NH$_3$ groups. Besides, CS is easy to dissolve in an acidic environment, which is the main reason for the limited adsorption capacity. When the pH value is higher than 4, the adsorption capacity of Cu$^{2+}$ increases significantly. As the pH of the solution increases, the number of hydrogen ions decreases, and protonation increases. There will be more adsorption sites on the surface of CS-MMT2, and the adsorption capacity will also show an increasing trend. At pH = 6, the adsorption capacity reached its peak and then began to decline. Cu$^{2+}$ will form Cu(OH)$_2$ precipitation at higher pH values. This shows from the side that the adsorption capacity of CS-MMT2 for Cu$^{2+}$ decreases. Therefore, pH = 6 is the best service condition for
CS-MMT. Compared with the montmorillonite adsorbent reported in the literature, the CS-MMT composite aerogel prepared in this experiment has a better adsorption capacity for Cu$^{2+}$.

### 2.6 Adsorption cycle performance

![Fig. 10 Circulation capability of CS-MMT2](image)

The regeneration efficiency of adsorbent is an important index to measure the actual use effect of an adsorbent. Generally speaking, effective adsorbent materials not only have high adsorption capacity but also have a great reuse effect. In this cycle experiment, we used a 0.2 mol/L EDTA solution as the desorption solution. The three-cycle effect of CS-MMT2 was measured. The experimental results are shown in Fig. 10. After 3 times of adsorption-desorption, the adsorption efficiency of CS-MMT2 aerogel changed slightly and remained at about 80%. EDTA mainly plays the role of chemically eluting Cu$^{2+}$ in the desorption process and has a certain group repair effect on CS-MMT2. CS-MMT2 aerogel can be regenerated during desorption and incomplete vacuum desorption. But at the same time, certain structural...
shrinkage and hole blockage are inevitable. This is due to the massive loss of CS-MMT surface groups during the adsorption and desorption process.

2.7 Discussion on adsorption principle

To explore the principle of adsorption, we characterized the adsorbed samples. As shown in Fig. 11(a), the C 1s spectra of CS-MMT2 were fitted with three components centered at 284.8, 285.9, 286.6, 287.7, and 288.4 eV, which can be assigned to C–C, C–N, C–O, C=O, and O=C=O, respectively. The emergence of a new characteristic peak at 934.4 eV, corresponding to the presence of Cu2p orbital. At the same time, the metal oxidation peak area was changed. Cu2+ reacted with the adsorbent to combine part of O. It is the oxygen-containing functional group that participates in the adsorption process. The Cu2p spin-orbit peaks showed that Cu2+ replaced the original hydrogen ion to form the corresponding complex. During the adsorption process, C–N, C–O, O=C=O content increased significantly, indicating that Cu2+ was successfully adsorbed on CS-MMT2. Therefore, it can be considered that the high adsorption capacity of CS-MMT2 to Cu2+ is due to chelating and stacking, and electrostatic attraction. As shown in Fig. 11(c), the intensity of the characteristic peak of the infrared spectrum changed to different degrees after copper ions were adsorbed, which indicates that amino, carboxyl, siloxane, and hydroxyl groups in CS-MMTS were involved in the
adsorption of Cu$^{2+}$.

3. Conclusions

CS-MMT composite aerogels were prepared by freeze-drying adsorption of Cu$^{2+}$. Montmorillonite has a layered structure. Modifier and physical methods are used to enlarge the distance between the montmorillonite, and CS is grafted on the surface of montmorillonite. The surface contains a large number of active sites, which promote the cross-linking of chitosan and montmorillonite, forming a stable three-dimensional network structure. The experimental results show that CS-MMT2 has good adsorption performance for Cu$^{2+}$. CS-MMT2 composite aerogel has a highly developed pore structure, high adsorption capacity, fast adsorption and desorption, and can effectively remove Cu$^{2+}$ with remarkable effect. MMT first provides adsorption sites through cation exchange, and the amino group on the surface forms hydrogen bonds with the hydroxyl group of the chitosan, which promotes the cross-linking of the chitosan and montmorillonite in the soil. After 3 times of adsorption-desorption, the removal effect of CS-MMT2 composite aerogel on Cu$^{2+}$ remains about 80%. A feasible method was provided for the selective removal and effective recovery of Cu$^{2+}$ from heavy metal wastewater.

4. Acknowledgment

This work was financially supported by the Key Research and Development Project of Jiangsu Province (BE2019734, BE2017151, BE2016171), the Major Program of Natural Science Fund in Colleges and Universities of Jiangsu Province(15KJA430005), the Program of Science and Technology of Suqian City (M201704, H201801, H201803), the National Natural Science Foundation of China (51702156, 81471183), the Program for Changjiang Scholars and Innovative Research Team in University (IRT_15R35), the Priority Academic Program Development of Jiangsu Higher Education Institutions and the Brand Major Program Development of Jiangsu Higher Education Institutions.
(PPZY2015B128). China Scholarship Council under Grant (No. 201908320194), the General Program of Natural Science Fund in Colleges and Universities of Jiangsu Province (19KJB430023), Scientific Research Starting Foundation of Nanjing Tech University, Science and technology innovation project for overseas of Nanjing City, Postdoctoral Science Foundation of Jiangsu Province (2019K005), the High-Performance Computing Center of Nanjing Tech University for supporting the computational resources, China Postdoctoral Science Foundation (2019M661781). Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of these programs.

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