

## A review of the removal of heavy metal ions in wastewater by modified montmorillonite

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### ABSTRACT

Heavy metal pollution in water environment has always been a hot issue in environmental pollution research. Among various removal methods of heavy metal pollution, adsorption has attracted attention because of its low cost and low secondary pollution. Montmorillonite is one of an ideal adsorption materials because of its natural pore structure and a high specific surface area. In this review, the modification methods of montmorillonite are introduced. The adsorption effect of different heavy metal ions and the main factors affecting the adsorption are discussed in detail. Meanwhile, the adsorption mechanism is intensively reviewed. The removal of Cr(VI), Cd(II), Pb(II), Cu(II), Cs(I), Co(II), Hg(II), Zn(II), Ni(II), and other nine heavy metal ions by modified montmorillonite was summarized and discussed, and the optimal pH values for different adsorbents were also different, but they were all less than 7, and the removal rates of heavy metal ions by modified montmorillonite under optimal conditions were all greater than 90%. It is concluded that the composite montmorillonite material has a great adsorption potential. Finally, it is proposed that the combination of advanced oxidation and composite montmorillonite material adsorption to remove heavy metal ions is an important direction of adsorption and removal of heavy metal ions in the water environment in the future.

**Key words:** Adsorption, Heavy metal ions, Modification technology, Montmorillonite

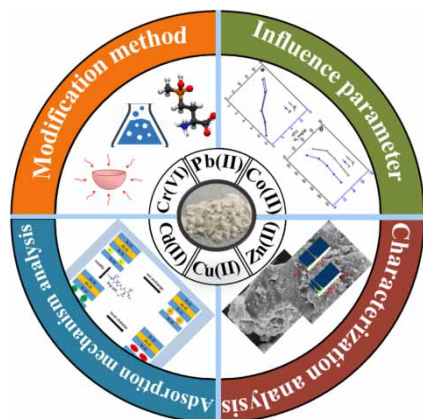
### HIGHLIGHTS

- Widely collected the domestic and foreign literature works on the modified adsorption of heavy metals by montmorillonite, and used the methods of analysis and synthesis to identify, classify, merge and study the original literature as a whole.
- The promising modification direction of montmorillonite and the key points of in-depth research in the removal of heavy metals were put forward.

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## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

After heavy metals enter the human body, they inhibit the activity of enzymes in the body, cause cytoplasmic poisoning, affect nerve tissue, and even damage the key organs of human detoxification function, endangering human health. Therefore, it has strict requirements on the concentration of various heavy metals in drinking water, as shown in Table 1. Unfortunately, many rivers, lakes, and seas in the world have been polluted by heavy metals to varying degrees. According to the survey, the average exposure concentrations of 10 typical heavy metals in the water bodies of the eight major river basins in China were generally high, and there were different degrees of heavy metal pollution, for example, Haikou Bay and Sanya Bay in Hainan, Chaohu Lake in Anhui, Jiaozhou Bay in the Shandong Peninsula, Songhua River in Changchun, etc., which all showed the compound pollution of multiple metal elements (Wei *et al.*, 2017; He *et al.*, 2019). The presence of moderate contamination of heavy metals in beach sediments along the Atlantic coast is potentially ecologically indicative of a low to moderate risk area for this coast (Ekoa Bessa *et al.* 2021). Moreover, in Association of Southeast Asian Nations (ASEAN), the development of chemical industries with inappropriate environmental management has

**Table 1** | The permissible limits of various toxic heavy metals in drinking water specified by various standards (mg/L) (Uddin, 2017).

Heavy metals	IS 10500	WHO	USEPA	EU Standard	MEP, China	CDW, Canada	NHMRC, Australia
Nickel	0.020	0.020	0.100	0.020	0.000	—	0.020
Lead	0.010	0.010	0.015	0.010	0.010	0.010	0.010
Zinc	5.000	3.000	5.000	—	—	5.000	—
Copper	0.050	2.000	1.300	2.000	1.000	1.000	2.000
Cadmium	0.003	0.003	0.005	0.005	0.005	0.005	0.002
Mercury	0.001	0.001	0.002	0.001	0.000	0.001	0.001
Arsenic	0.010	0.010	0.010	0.010	0.050	0.010	0.010
Chromium	0.050	0.050	0.100	0.050	0.050	0.050	0.050
Iron	0.300	0.200	0.300	0.200	—	0.300	—

led to an increasing trend of heavy metal pollution. This has led to transboundary pollution of heavy metals in some border areas, which seriously affects the daily life of people (Ding, 2019).

At present, there are many treatment methods for heavy metal pollution in water, which are mainly divided into the following two categories: physico-chemical and biological methods. Physical-chemical methods include chemical precipitation, oxidation-reduction, electrochemical, membrane separation, ion exchange, and adsorption, etc.; and biological methods mainly include phytoremediation and biological flocculation. The adsorption method is characterized by simple operation, wide sources of adsorption materials, and a wide application range. It is considered to be one of the most effective and promising treatment methods for heavy metal pollution in water. Adsorption material is an important factor affecting the treatment of heavy metal pollution by adsorption. The composite material with activated carbon, graphene, biochar, and double-layer hydroxide (LDH) as the carrier has attracted widespread attention (Huang *et al.*, 2017; Li *et al.*, 2017; Dou *et al.*, 2018). However, the high cost, complexity, and synthesis hazards of adsorbent materials may limit their utilization. Therefore, it is of a great significance to study cheap adsorbent materials with a reasonable adsorption efficiency. Montmorillonite (MMT) composite material has the advantages of complex structure and adsorption characteristics, its unique structure, low cost, and abundant reserves. It can also be used as an adsorbent itself to remove heavy metal ions from aqueous solutions (Yang *et al.*, 2020). The main purpose of this review is to provide detailed information on natural or modified forms of MMT and its excellent adsorption properties on various toxic heavy metals in an aqueous solution. In the previous reviews, the research object categories were many but not specific enough, involving various types of clays and clay mineral complexes, and the removal mechanism of heavy metal ions adsorbed by modified MMT was not studied deeply enough, mostly for the removal effect. There is a new class of composites based on MMT for the removal of heavy metal ions from aqueous solutions; however, this class of adsorbents has not been discussed in the literature. In this paper, the literature on the modified adsorption of heavy metals by MMT at home and abroad was extensively collected, and the original literature was identified, classified, merged, and studied as a whole using the analytical synthesis method, and various modification methods, removal effects, influencing factors, and adsorption mechanisms of modified MMT were summarized and generalized, and finally, further perspectives on the adsorption and removal of heavy metal ions by MMT were proposed.

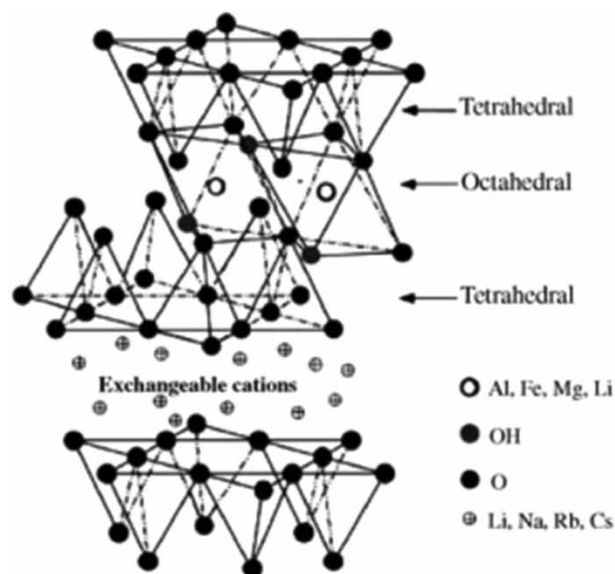
## 2. MMT PROPERTIES AND MODIFICATION METHODS

### 2.1. The structure and properties of MMT

MMT is a 2:1 type layered aluminosilicate. It is a unit composed of two siloxy tetrahedral flakes and one aluminum octahedral flake. The overall structure is dioctahedral (Brigatti, 2013), as shown in Figure 1. The tetrahedral and octahedral flakes are combined in such a way that the tetrahedral tip of each silica flake and a hydroxyl layer of the octahedral flake form a common layer, and the atoms in this layer are shared by the two layers. Therefore, MMT belongs to the three-layer clay mineral.

Its general formula is  $(M^+, M_{1/2}^{2+})_{x+y}(Y_{2-y}^{3+}, Y_y^{2+})(Si_{4-x}, Al_x)O_{10}(OH)_2 \cdot nH_2O$ , where M and Y represent the cations in the interlayer and octahedron, respectively. Second, the substitution of isomorphous cations in the type 1 structure generates negative charges on the square plane. This negative charge is compensated by the interlayer cations. The thickness of the main layer is 0.96 nm (Dalhat *et al.*, 2018). The cation exchange reaction is rapid, Na(I), Ca(II), and other cations from the outer spherical surface complex. The cations in the solution are easily ion-exchanged, so that heavy metal ions can adsorb between the MMT layers (Yang *et al.*, 2015).

MMT is receiving more and more attention due to its natural nanostructure, high specific surface area, abundant active centers, high physical and chemical stability and cation exchange capacity, and various morphological advantages such as interlayer space for hybridization with different species.



**Fig. 1** | Schematic diagram of the MMT structure (Ray & Okamoto, 2003). Copyright 2003, Elsevier.

## 2.2. Modification method of MMT

MMT is very suitable for adsorbing heavy metal ions in wastewater due to its negative surface. However, the structure of MMT is very compact, water is easily adsorbed in the interlayer area of the adsorbent, and the ions in the solution enter the interlayer of MMT and are blocked, which limits the adsorption capacity of MMT to a certain extent (Atasoy & Bilgic, 2017). In order to increase the adsorption performance of MMT for heavy metals, it is necessary to modify the MMT to improve its adsorption capacity. The modification methods of MMT mainly include physical and chemical modification (HongYan *et al.*, 2020). The commonly used modification methods are as follows: (1) acid activation, heat treatment (Bibi *et al.*, 2014; Biswas *et al.*, 2016); (2) organic modification (Wang *et al.*, 2017); and (3) inorganic modification (Zhang *et al.* 2017a). These modification methods were sometimes used in combination.

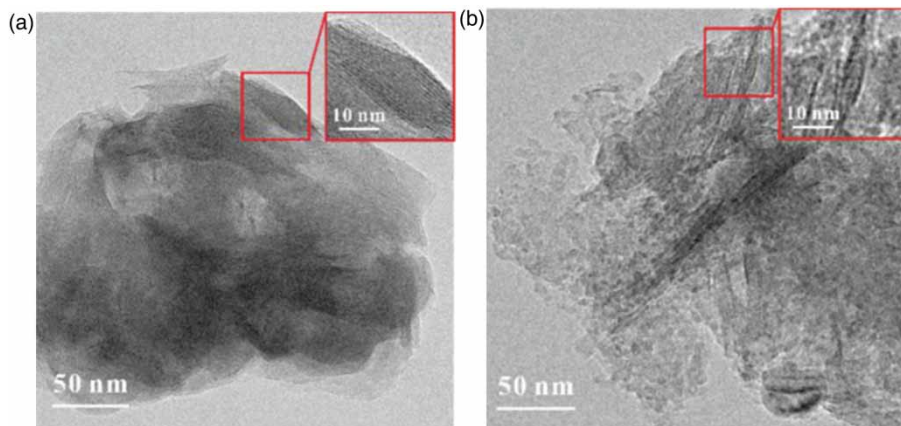
### 2.2.1. Acid activation

Acid activation refers to the treatment of minerals with high concentrations of inorganic acids, which can destroy the natural MMT structure to give it a well-developed pore structure, and is one of the most effective methods to prepare materials with higher acidity and better adsorption properties. Usually, high-concentration hydrochloric acid and sulfuric acid are used for acid activation of MMT, so that while the MMT is partially dissolved, it can also remove mineral impurities and leaching part of the scaling elements. After the MMT undergoes acid activation treatment, hydrogen ions replace the natural exchangeable cations in MMT and penetrate into the interlayer of MMT to corrode the OH groups, thus changing the surface properties and acidity characteristics of MMT (Komadel, 2016; Pentrák *et al.*, 2018). Bhattacharyya & Gupta (2008) used 0.25 mol/L  $H_2SO_4$  to acid activate the MMT, which increased the distance between the MMT layers, decreased the strength, increased the specific surface area and voids on the crystal structure. It was confirmed that acid activation increased the adsorption capacity of MMT and improved the adsorption performance of MMT for Cd(II) (Bhattacharyya & Gupta, 2008). Yang *et al.* (2020) used acid-activated organic montmorillonite (AOMt) to convert the Si-O tetrahedral

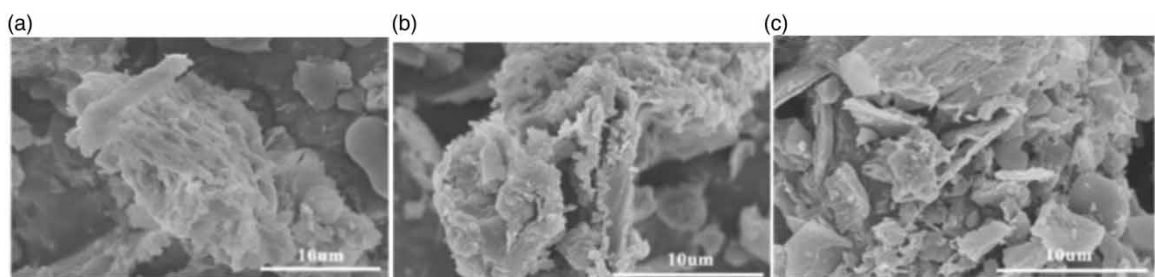
structure lacking functional groups into nano-silica (PNS) with a large number of hydroxyl functional groups and porous structures. X-ray diffraction (XRD) analysis of montmorillonite (OMt) showed that the OMt lattice fringes were obvious before acid activation, indicating that it has a higher degree of crystallinity. Irregular morphology was observed after AOMt acid activation, confirming the formation of amorphous PNS, as shown in Figure 2 (Yang *et al.*, 2020).

### 2.2.2. Heat treatment

Heat treatment is done to remove hydroxyl groups by heating, which can change its structure and surface properties and further improve its adsorption performance. Song *et al.* (2019) modified MMT-biochar composites by 200 °C hydrothermal method and 350, 500, and 700 °C high-temperature pyrolysis method. The obvious differences before and after the thermal activation can be found by SEM image as shown in Figure 3. The morphology of the biochar treated with higher temperatures changed greatly after being treated with MMT. The modified composite material was used to remove Zn(II) ions in the solution. The experimental results proved that the adsorbent had the fastest adsorption rate at 700 °C (Song *et al.*, 2019). Irawan *et al.* (2019) prepared magnetic nanoparticles-coated MMT composites by a one-pot solvothermal method and the adsorption capacity of the composite material was four times that of natural MMT (Irawan *et al.*, 2019). Wei *et al.* (2018)



**Fig. 2** | SEM images of organic MMT acid before and after activation: (a) OMT and (b) AOMt. Copyright 2020, Elsevier.

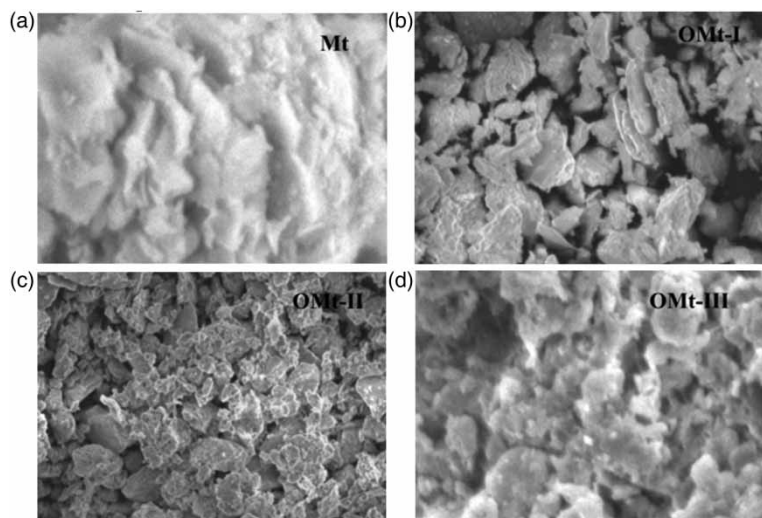


**Fig. 3** | SEM images of MMT-biochar before and after thermal activation: (a) 200 °C; (b) 500 °C; and (c) 700 °C (Song *et al.*, 2019). Copyright 2019, Elsevier.

used 100 °C drying, 200 °C calcination, 300 °C calcination, and freeze-drying to process sodium-based MMT (Na-MMT). The experimental results proved that the adsorption effect of Na-MMT with different pretreatment methods on Cd(II) also differed, and the adsorption capacity of 300 °C calcined modified Na-MMT was the largest ( $Q_{\max} = 11.1 \text{ mg/g}$ ) (Wei *et al.*, 2018).

### 2.2.3. Organically modified

Organic modification of MMT is to replace exchangeable cations (mainly sodium, calcium and other cations) between MMT layers by organic molecules, organic functional groups, through ion exchange. Organic modifiers also increase the MMT layer spacing and surface functional group content, leading to a significant increase in the adsorption of MMT. There are many kinds of organic substances that can be used for exchange, such as chitosan, surfactant, lignin polyacrylic acid, quaternary ammonium salt with long alkyl chain and so on (Hongjia *et al.*, 2019). Tsai *et al.* (2016) used chitosan/montmorillonite (CTS-MMT) composite microbeads as adsorbents to remove Cu(II), Ni(II), Zn(II), and Pb(II) in aqueous solution, kinetic rates and adsorption capacities of heavy metal ions are increased in polymetallic ion coexistence systems (Tsai *et al.*, 2016). Jemima *et al.* (2018) modified MMT with a series of biodegradable cationic ester surfactants, and the obvious difference between before and after the organic modification can be found through the SEM image. The natural MMT surface aggregates in a plate shape, and the addition of surfactant makes its surface crown-like, which leads to an increase in specific surface area and porosity, and also confirms that the surfactant is partially intercalated between the MMT layers, as shown in Figure 4. The adsorbent is used to adsorb Cr(VI) ions in the aqueous solution. Studies have shown that the adsorption performance of organically modified montmorillonite is better than that of natural MMT, and as the hydrophobic chain length of cationic surfactants increases, the adsorption performance of the adsorbent becomes greater. (Jemima *et al.*, 2018). Jian-ping *et al.* (2021) prepared a new adsorbent by combining carboxymethyl chitosan with natural MMT for the removal of Cu(II), Zn(II), Pb(II), Cd(II), and Cr(VI) mixed heavy metal ions; the surface morphology and structure of the adsorbent were analyzed by characterization means, and the results showed that the surface area of the modified MMT increased, the crystal layer spacing

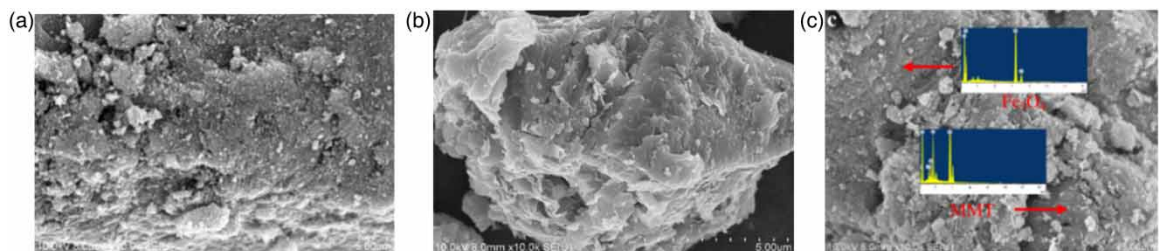


**Fig. 4** | SEM images of MMT before and after surfactant modification: (a) Mt; (b) OMT-I; (c) OMT-II; and (d) OMT-III (Jemima *et al.*, 2018). Copyright 2018, Springer Nature.

increased, and the adsorption performance improved significantly. The results showed that the surface area of the modified MMT increased, the crystal layer spacing increased, and the adsorption performance was significantly improved (Jian-ping *et al.*, 2021). Ma *et al.* (2017) combined lignin polyacrylic acid (LBP-AA) prepared by copolymerization of lignin and acrylic acid (AA) with organic MMT to obtain nanocomposites. Studies have shown that grafting of lignin and organic MMT not only contributes to the formation of pores, but also serves to fill and support them. It can quickly and feasibly remove Pb(II) in sewage and has potential application prospects (Ma *et al.*, 2017). Yaxin *et al.* (2017) prepared a novel adsorbent by organic modification of the cationic surfactant cetyltrimethylammonium bromide (CTMAB) and the ammonia carboxylate complexing agent disodium ethylenediaminetetraacetic acid (EDTA) as modifiers for the removal of high-concentration wastewater in the concentration range of 50–500 mg/L. It is shown that the adsorbent has the best adsorption effect under medium alkaline conditions (Yaxin *et al.*, 2017).

#### 2.2.4. Inorganic modification

Inorganic modification is to use the ion exchange and swelling properties of MMT under the action of a strong polar solvent and introduce an inorganic pillaring agent between its layers to make the dispersed MMT flakes form a columnar layered structure and increase the layer space and specific surface area, which can absorb and hold more pollutant molecules. With the insertion of the inorganic pillaring agent and the introduction of a large number of active hydroxyl groups, increases its acidic sites and enhances its stability, thus changing the adsorption capacity of MMT in wastewater. Zheng *et al.* (2017) synthesized ammonium pillared modified  $\text{Fe}_3\text{O}_4$ /MMT composite material and analyzed the SEM image. As shown in Figure 5, the  $\text{Fe}_3\text{O}_4$  surface is rough and agglomerated, and the MMT has a layered structure and the surface is relatively smooth. There is no significant change in the structure after the combination of the two (Zheng *et al.*, 2017). Almasri *et al.* (2017) prepared a hydroxy-iron-modified montmorillonite (HyFe–MMT) composite material by a wet chemical method, which was used to remove heavy metal ions As(III) in the aqueous solution. The adsorption capacity of natural MMT is increased to more than 5 times of the original capacity after modification by this method, after the adsorbent is put in, the removal rate of As(III) exceeds 55% in the first 30 s, and it is quickly adsorbed within 15 min, and the removal rate is as high as 90%. In the experiment, the residence time in the batch treatment system is only 1–2 min, which can treat more contaminated water at the same time, thereby saving costs (Almasri *et al.*, 2018). Mnasri-Ghnmimi & Frini-Srasra (2019) studied the application of single-layer pillared clay and mixed pillared clay to adsorb heavy metal ions Cd(II), Co(II), and Cu(II). It is proved that laminated clay can adsorb metals with higher affinity than that of non-laminated clay (Mnasri-Ghnmimi & Frini-Srasra, 2019).

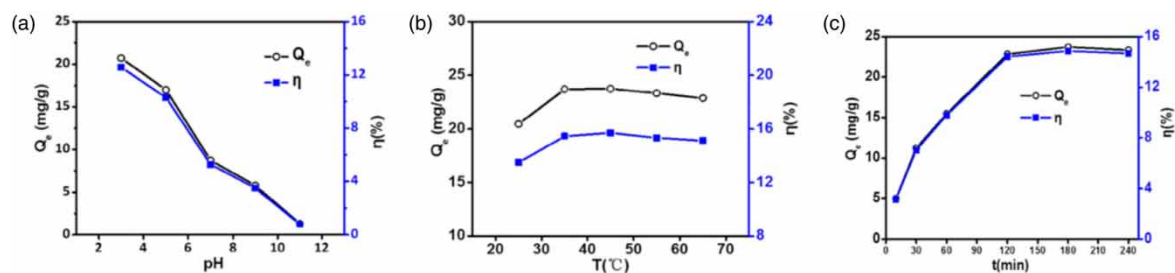


**Fig. 5** | SEM images of MMT before and after inorganic modification: (a)  $\text{Fe}_3\text{O}_4$ ; (b) MMT; and (c) MMT/ $\text{Fe}_3\text{O}_4$  (Jian-ping *et al.*, 2021). Copyright 2017, Elsevier.

### 3. RESEARCH PROGRESS OF MODIFIED MMT IN THE TREATMENT OF HEAVY METAL POLLUTION

#### 3.1. The removal effect of modified MMT on heavy metal chromium

Wu *et al.* (2015) inserted nano-zero-valent iron (NZVI) between the MMT layers to prepare nano-zero-valent iron/montmorillonite (NZVI/MMT) composite materials, which are used to remove heavy metal ions Cr(VI) from aqueous solutions. It was shown that NZVI/MMT was significantly more stable in the removal of Cr(VI) than the carrier NZVI, and its reactivity was less dependent on the pH value. The adsorbent had a good removal ability in the range of pH 3–6. The maximum adsorption capacity is 15 mg/g (Wu *et al.*, 2015). Cai *et al.* (2017) used the anionic surfactant sodium dodecyl sulfate (SDS) to organically modify montmorillonite (MMT) to obtain SDS-MMT, and the introduced cellulose acetate (CA) was prepared under the modulation of electrostatic spinning system to obtain electrospun cellulose organically modified MMT nanocomposites. The adsorption experiment showed that the adsorbent has a higher adsorption performance for Cr(VI) in the aqueous solution. Solution pH, temperature, and contact time have an effect on the adsorption of heavy metal ions by the adsorbent. As shown in Figure 6, the adsorption capacity will decrease significantly with the increase of pH. The adsorption performance is best when the pH is 3 (Cai *et al.*, 2017). Yu *et al.* (2016) prepared chitosan (CS)/reduced graphene oxide (rGO)/montmorillonite (MMT) porous composite hydrogels by modifying MMT with chitosan (CS) and reduced graphene oxide (rGO) to remove Cr(VI) from aqueous solutions. The adsorbent can return to its original shape and size like a sponge after compression and deformation and exhibits good stability under acidic conditions. When the pH value is 2, it adsorbs the best effect, and the maximum adsorption capacity is as high as 87.03 mg/g at 288 K, and the composite porous hydrogel can be repeatedly used as adsorbent, and the removal efficiency of Cr(VI) by the adsorbent can still be maintained at 98.9% of the initial absorption rate after four cycles (Yu *et al.*, 2016). The cell wall of Arbuscular Mycorrhizal Fungi (AMF) spores contains functional groups such as hydroxyl, amino, and carboxyl groups coordinated with metal ions. Sathvika *et al.* (2018) solidified the spores of AMF on the surface of MMT, and the biosorbent is prepared to remove Cr(VI) from the aqueous solution. The adsorbent has a strong adsorption capacity for Cr(VI) in the pH range of 2–3, and its maximum adsorption capacity is 11.185 mg/g (Sathvika *et al.*, 2018). Wei *et al.* (2019) prepared carbon-coated MMT nanocomposite (CMT) by hydrothermal carbonization of MMT, which was used to remove Cr(VI) in an aqueous solution. The adsorption capacity changed significantly at different pH values. When pH is 2, the maximum adsorption capacity is 100 mg/g, when pH is 8, the adsorption capacity is only 12.4 mg/g, but it is still greater than the adsorption capacity of some clay minerals and other solid adsorbents at pH 2, so CMT can be used for a wide range of pH values (Wei *et al.*, 2019). Xiaojiang *et al.* (2019) used polyhydroxy aluminum to provide an Al source combined with cetyl pyridinium bromide (CPDB)-modified sodium MMT to remove 10 mg/L of



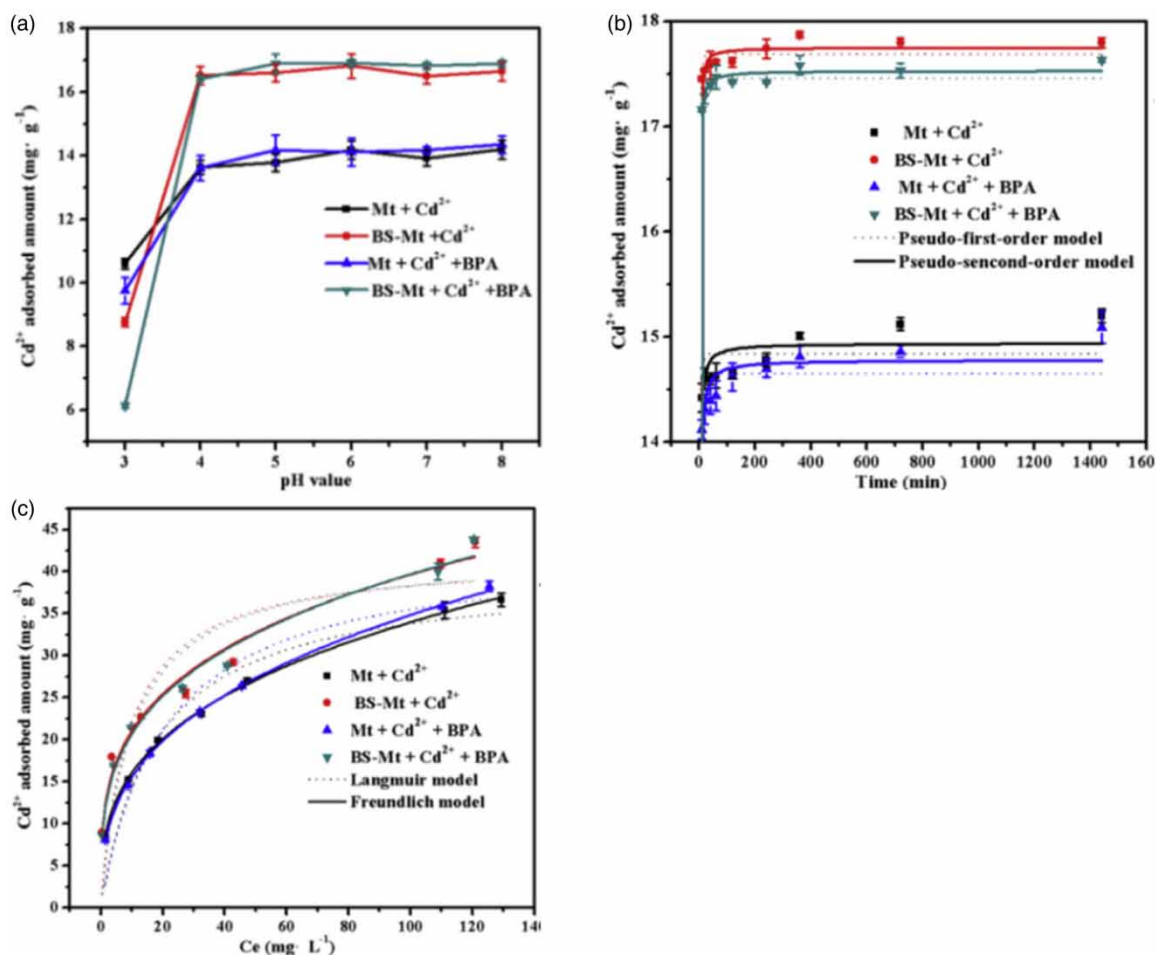
**Fig. 6** | The effect of organically modified MMT nanocomposites for removing heavy metal ions such as Cr(VI): (a) pH; (b)  $T$  ( $^{\circ}\text{C}$ ); and (c)  $t$  (min) (Cai *et al.*, 2017). Copyright 2017, Elsevier.



chromium-containing wastewater. The results of the study measured that the removal rate of Cr(VI) by the adsorbent reached 98.55%, which improved the adsorption performance of MMT (Xiaojiang *et al.*, 2019).

### 3.2. Removal effect of modified MMT on heavy metal cadmium

Chen *et al.* (2015) used two modified MMTs, Na-MMT and calcium-based MMT (Ca-MMT), to adsorb Cd(II) in water through batch adsorption experiments. The Cd(II) in the water sample was within 10 min of adding Na-MMT Cd(II) in the water sample added with Ca-MMT cannot be completely removed regardless of the contact time. The adsorption capacity of Na-MMT for Cd(II) measured by the experiment is 0.204 mmol/g, and the treatment effect of Na-MMT composite material on heavy metal ions is better than that of Ca-MMT. The adsorption processes of the two modified MMTs are in following the quasi-second-order kinetic equation (Chen *et al.*, 2015). Taha *et al.* (2017) studied the applicability of natural Na-MMT to remove heavy metal ions Cd(II) under acidic conditions and explored influencing factors such as pH, contact time, and initial concentration. As the pH value of the solution increases, the adsorption capacity gradually increases. When the pH value is 2.0, the removal rate of heavy metal ions Cd(II) is 75.59%, and when the pH value increases to 7, the removal rate is as high as 95.11%. In addition, the removal rate will be reduced. With the increase of the initial concentration of Cd(II), the adsorption capacity of Na-MMT increases with the increase of the initial concentration of heavy metal ions Cd(II). The reason is that the proportion of heavy metal ions in the solution far exceeds the active sites of the adsorbent. The binding competition between ions and active sites is fierce. As the ion concentration increases, the adsorption-desorption equilibrium is gradually reached. The ions are adsorbed by the pores and the adsorption volume of the adsorbent material increases. The adsorption rate of Na-MMT is within the first 30 min. It is very rapid, and then gradually decreases until equilibrium is reached. The best adsorption time of Na-MMT for Cd(II) is 30 min. The reason is that as the active center is gradually occupied, the adsorption rate of metal ions from the surface to the micropores slow downs, and when the adsorbent surface and micropores are saturated with their respective metals, the removal efficiency is basically constant (Taha *et al.*, 2017). Liu *et al.* (2017) adsorbed Cd(II) in an aqueous solution by nano-montmorillonite (NMMT). It was shown that the removal rate of Cd(II) increased with the increase of pH and contact time and decreased with the increase of initial metal ion concentration, and the maximum adsorption capacity of the adsorbent was 17.61 mg/g, and the desorption efficiency of Cd(II) by simulating acid rain is 1%, indicating that NMMT has stable and good adsorption performance (Liu *et al.*, 2017). Liu *et al.* (2016) prepared octadecyl dimethyl betaine (BS-18)-modified montmorillonite (BS-MMT) using amphoteric surfactants to remove Cd(II), and the removal effect is shown in Figure 7. The adsorption capacity of BS-MMT increases with the increase of pH value, and tends to balance at pH 4, and it adsorbs quickly to Cd(II) and reaches equilibrium at a contact time of 5 min. Compared with natural MMT, its maximum adsorption capacity is increased (Liu *et al.*, 2016). Elsherbiny *et al.* (2017) modified MMT by polyaspartate to prepare composite material polyaspartic acid-montmorillonite (IPS) to adsorb Cd(II) in water. The adsorption capacity of the composite material for Cd(II) is 67.57 mg/g, which is 29.84% higher than the adsorption capacity of Na-MMT before modification. The thermodynamic parameters indicate that the heavy metal ion adsorption process is a spontaneous exothermic process (Elsherbiny *et al.*, 2017). Yan *et al.* (2019) introduced extracellular polymer (EPS) loaded on MMT to prepare EPS-MMT to adsorb Cd(II), and changed the mass ratio of EPS to MMT to obtain the maximum adsorption capacity. The experiment showed that the mass ratio was 0.5:50. The maximum adsorption capacity is 74.8 mg/g, and the adsorption capacity of EPS–MMT composite material for Cd(II) is better than that of natural MMT. The lower the mass ratio, the higher the adsorption capacity of composite material for Cd(II) (Yan *et al.*, 2019).

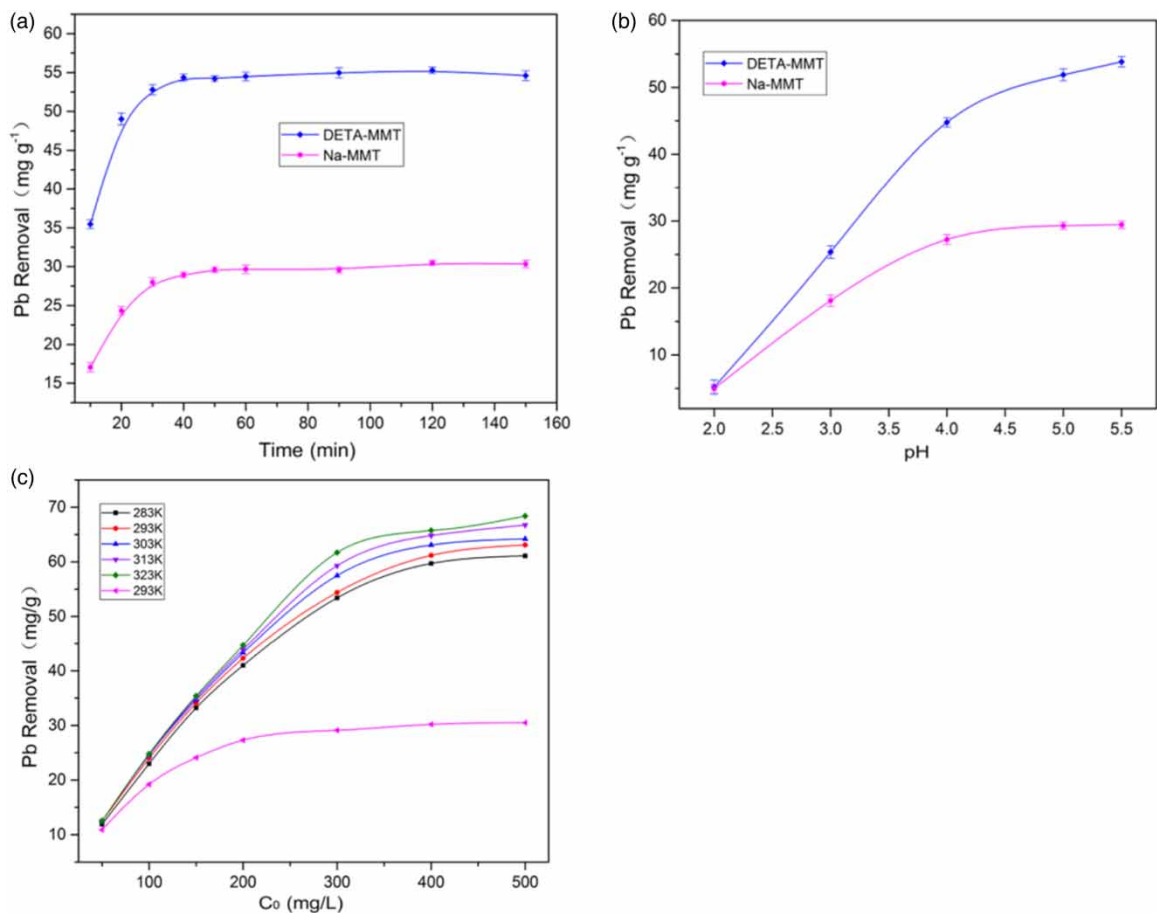


**Fig. 7** | The effect of organically modified MMT nanocomposites for removing heavy metal ions such as Cd(II): (a) pH; (b)  $T$  (min); and (c)  $C_e$  (mg/L) (Liu *et al.*, 2017). Copyright 2017, Springer Science + Business Media B.V.

### 3.3. The removal effect of modified MMT on heavy metal lead

Mittal *et al.* (2015) prepared biopolymer-based nanocomposites using L-cysteine-modified MMT loaded with sodium alginate to remove heavy metal ions Pb(II), and the ion adsorption capacity of the composite materials increased rapidly within 30 min and slowly reached saturation at about 120 min. The adsorption capacity increases with the increase of the pH of the solution (Mittal *et al.*, 2015). Adraa *et al.* (2017) found that the cysteine-modified MMT composite materials had better adsorption performance for Pb(II) than natural MMT, due to the strong ability of the composite material to chelate heavy metal ions (Adraa *et al.*, 2017). Datta *et al.* (2017) used tri-n-octylamine-modified MMT to adsorb heavy metal ions Pb(II). Compared with natural MMT, the adsorption capacity of modified MMT increased from 3.37 to 33.1 mg/g. The adsorption capacity increases with the increase of the initial ion concentration. Through the study of adsorption kinetics, the removal rate of Pb<sup>2+</sup> ions by MMT (0.1 g) and MMT-TOA (0.01 g) was measured to reach 81.42% and 80.67% at 100 and 80 min, respectively. Also it can be seen that the adsorption capacity of MMT-TOA is greatly improved compared

with MMT (Datta *et al.*, 2017). Wang *et al.* (2018) prepared the composite material DETA-MMT, which doubled the specific surface area of DETA-MMT compared with Na-MMT, resulting in a strong adsorption and immobilization of Pb(II). The maximum adsorption capacity of the adsorbent was 61.1 mg/g, which was twice the adsorption capacity of Na-MMT. The adsorption capacity was affected by the pH value. When the pH value increased from 2 to 4, the adsorption capacity of Na-MMT and DETA-MMT for Pb(II) both increased rapidly, mainly due to the competition of Pb(II) with a large amount of H<sup>+</sup> for adsorption sites under the condition of strong acid solution. When the pH was 5.5, H<sup>+</sup> amount in the solution was reduced, so the maximum adsorption capacity was reached. The experimental results showed that the higher the pH of the adsorbent in the acidic solution, the better the removal of Pb(II), as shown in Figure 8 (Wang *et al.*, 2018). Anam & Rais (2018) successfully synthesized a new type of biodegradable yellow collagen/montmorillonite (XG/MMT) bio-nano composite to remove heavy metal ions Pb(II) in industrial wastewater. Under the optimal reaction conditions, the maximum adsorption capacity of the adsorbent is 187.08 mg/g, and it can be successfully used in 0.05 M hydrochloric acid solution until the fifth cycle, and the adsorption rate can still meet the demand, and it can be successfully



**Fig. 8** | The effect of organically modified MMT nanocomposites for removing heavy metal ions such as Pb(II): (a)  $T$  (min); (b) pH; (c)  $C_0$  (Wang *et al.*, 2018). Copyright 2020, Elsevier.

used up to the fifth cycle in the 0.05 M hydrochloric acid solution, and the adsorption rate can still meet the demand (Anam & Rais, 2018). Zhang *et al.* (2019) prepared composite material montmorillonite-graphene oxide (MGC) to remove heavy metal ions Pb(II). In a single adsorption experiment, the removal rate of Pb(II) reaches 98.23%, and when pH was 2–6, the removal rate increases with the increase of pH. The higher pH, the lower the degree of protonation, and weaker the H<sup>+</sup> competition in the solution, which was more beneficial for the adsorption of Pb(II) on MGC (Zhang *et al.*, 2019). Zhu *et al.* (2019) loaded lysine (L-Lysine) between the layers of Na-MMT to prepare lysine-modified montmorillonite (L-MMT) against heavy metal ions Pb(II) adsorption. The study found that when the pH value is low, the adsorption capacity of the adsorbent to Pb(II) the solution is small. As the pH value increases, the adsorption capacity increases rapidly, and the maximum adsorption is reached at pH = 5.5. The reason is that when the pH value is low, the H<sup>+</sup> concentration in the solution is large, and there is competitive adsorption between it and the heavy metal ion Pb(II) in the solution. The maximum adsorption capacity of lysine-modified montmorillonite (L-MMT) for heavy metal ions Pb(II) at room temperature is 43.3 mmol/100 g, which is significantly higher than the maximum adsorption capacity of Na-MMT of 15.3 mmol/100 g (Zhu *et al.*, 2019). Ma *et al.* (2019) prepared LS-MMT to remove heavy metal ions Pb(II) from the solution by modifying MMT with sodium lignosulfonate (Na-LS). Experiments show that the adsorption capacity of LS-MMT is higher than that of natural MMT. The pH value has a great influence on the adsorption capacity of the adsorbent. When the pH value is 5, the adsorption capacity of the adsorbent can reach 124.15 mg/g (Ma *et al.*, 2019). Chen *et al.* (2020) prepared tourmaline-montmorillonite (TMMs) composites by vacuum sintering to adsorb heavy metal ions Pb(II) in water and explored the adsorption properties of the composites at different sintering temperatures and different tourmaline ratios. The results shows that the adsorption performance is the best when the sintering temperature is 800 °C and the proportion of tourmaline is 30.7%, and the maximum adsorption capacity is 303.21 mg/g. In addition, TMMs have a wide range of pH applications. When the pH value is 3.0, the adsorption rate reaches 78.5%; with the increase of pH value, when the pH value increases to 4.0, the adsorption rate is as high as 99%. The adsorption efficiency remains stable within the pH range of 4.0–6.0. Its stability benefits from the ability of tourmaline (TM) to buffer pH (Chen *et al.*, 2020).

### 3.4. The removal effect of modified MMT on other heavy metals

Kalantari *et al.* (2015) prepared Fe<sub>3</sub>O<sub>4</sub>/MMT nanocomposites. Low-concentration adsorbent (0.08 g/0.025 L) treated 182.94 mg/L of Cu(II) solution, and the removal rate can be as high as 94.89% within 120 s, and it has a strong and efficient adsorption capacity (Kalantari *et al.*, 2015). Zheng *et al.* (2017) modified Fe<sub>3</sub>O<sub>4</sub>/MMT composites with ammonium pillars to remove Cs(I) in the aqueous solution. The experiment found that the adsorption capacity of the composites has an almost linear relationship with the initial concentration, which increases with the increase of the initial concentration. A large and good removal effect was observed in the pH range of 4–10, reaching a maximum value of 37.5 mg/g at pH 11, and high selectivity to Cs(I) is seen when ions coexist (Zheng *et al.*, 2017). Wang *et al.* (2014) prepared composite material CTS–MMT with chitosan (CTS)-modified MMT to remove heavy metal ions Co(II), and it was observed by XRD that the distance between MMT layers increased indicating that CTS has been inserted into the MMT, changing the mass ratio of CTS/MMT to improve the adsorption performance of the adsorbent. Studies have shown that Co(II) has multilayer adsorption on the composite material, and its maximum adsorption capacity is as high as 150 mg/g (Wang *et al.*, 2014). Cai *et al.* (2017) used Ca-MMT adsorption to remove Cu(II) wastewater with a concentration range of 10–160 mg/L. The results showed that under acidic conditions, the higher the initial pH of the solution, the higher the Cu(II) removal rate. The removal rate is more than 93% (Yueshen *et al.*, 2018). Hwab *et al.* (2019) prepared chitosan-modified MMT (HPFC/MS-S) with sulfhydryl-modified MMT and carboxymethyl chitosan to

remove the pollutant Hg(II) in the aqueous solution and found that the removal effect of the adsorbent in a strong acid environment is still greater than 90%, and the reaction efficiency reaches 80% within 5 min, and the adsorption capacity under optimal conditions is as high as 1,875 mg/g, its adsorption capacity can be used as a potential, alternative, and cost-effective adsorbent (Hzab *et al.*, 2019). Zhang *et al.* (2017b) prepared lignin-montmorillonite (L-MMT) nanocomposite as a reusable adsorbent for Co(II). LMT has a good adsorption effect on Co(II), and the adsorbed Co(II) is easily desorbed by nitric acid, and the nanocomposite material can be reused four times, and the adsorption performance will not be significantly reduced (Zhang *et al.*, 2017b). Sun *et al.* (2019) used organic lignin and MMT to prepare an adsorbent for removing Cu(II). Its maximum adsorption capacity is 1.17 mmol/g. The adsorbent has excellent regeneration performance, and the desorption rate is greater than 0.8. The regeneration rate after the second time is still greater than 80%, and it has good desorption performance and repeated use performance (Sun *et al.*, 2019). Liu *et al.* (2019) used surfactants, namely octadecyl-trimethyl-ammonium chloride (STAC) and ethylenediamine (En) to prepare organically modified MMT STAC–En–MMT. Under the interference of PNP, Cu(II) and Zn(II) are adsorbed at the same time. The study found that the adsorption capacity of the adsorbent increases with the increase of pH, and the adsorption performance increases slightly with the increase of temperature. After repeated use, the adsorption performance of the adsorbent is also very good, and the maximum adsorption capacities of STAC–En–MMT in the presence of Cu(II), Zn(II), and PNP are 174.53 and 37.15 mmol/kg, respectively (Liu *et al.*, 2019). Sani *et al.* (2017) prepared high-efficiency nanocomposites with MMT-loaded nano-zinc oxide (ZnO) for the adsorption of heavy metals Cu(II) and studied the effect of zinc oxide on improving the removal of Cu(II) from aqueous solutions by nanocomposites. In the role of ion adsorption efficiency, the nano-zinc oxide is inserted between the MMT layers to generate additional active centers, thereby enhancing the pore structure and surface area. The removal rate of Cu(II) by the adsorbent will increase with the increase of pH value, and the removal rate can reach 98% in the range of 4–6 (Sani *et al.*, 2017). Moreno-Sader *et al.* (2019) introduced high molecular polymer polyacrylamide (PAM) to prepare polyacrylamide-sodium montmorillonite (PAM–MMT) to remove heavy metals Co(II) and Ni(II). The study showed that when the pH value is 6, the removal rate of the adsorbent for 100 ppm Ni(II) solution is as high as 99.3%, and the removal rate for 60 ppm Co(II) solution is as high as 98.7%, which are higher than Na-MMT under the same conditions (Moreno-Sader *et al.*, 2019). Kenawy *et al.* (2019) used melamine (MEL) to modify chitosan–montmorillonite (CS–MMT) to synthesize a new nanocomposite material MEL–CS–MMT, which is used to adsorb Fe(III) in the solution. Under the reaction conditions, the maximum adsorption capacity of the adsorbent is as high as 154.32 mg/g. Compared with other adsorbents, it has a higher adsorption capacity. It can show higher removal efficiency and selectivity in the presence of multiple coexisting ions. The adsorbent can be repeatedly used for three times and verified for the recovery potential of the prepared nanocomposite (Kenawy *et al.*, 2019). Abdulla *et al.* (2013) modified Na-MMT with arginine to prepare Arg-MMT to adsorb Cu(II) in the aqueous solution. Because of the strong acid medium (pH < 3), the adsorption material at the hydrated surface is protonated. Excessive H<sup>+</sup> will compete with heavy metal ions to occupy active sites. With the increase of pH, the surface protons will be removed, and the surface will be more negatively charged. The heavy metal ions Cu(II) and the adsorption material increases the electrostatic attraction. When the pH value is 5, the maximum adsorption capacity of the adsorbent to Cu(II) is 29.15 mg/g. Experiments show that the higher the pH value, the better the adsorption effect. The adsorption capacity increases with the increase of the initial Cu(II) concentration, and gradually reaches equilibrium (Abdulla *et al.*, 2013; Chu *et al.*, 2020).

## 4. ANALYSIS OF THE REMOVAL MECHANISM OF MODIFIED MMT

### 4.1. Ion exchange

MMT mainly removes heavy metal ions through cation exchange. When the Fe<sub>3</sub>O<sub>4</sub>/MMT composite material is modified by ammonium pillaring to remove Cs(I) in the aqueous solution, it is found that pH and coexisting

cations have a great influence on the composite material. They affect interlayer cations by the ion exchange process between Cs(I) and interlayer cations (Zheng *et al.*, 2017). The removal mechanism of heavy metal ions by Na-MMT and Ca-MMT is not exactly the same. Ion exchange is the main mechanism of Ca-MMT. For Na-MMT, ion exchange plays a more important role at relatively a low pH. When the pH value is high, precipitation is the main mechanism (Chen *et al.*, 2015). This is consistent with the conclusion that the ion exchange of the adsorbent Na-MMT is the main reason for absorbing heavy metal ions. Na-MMT is modified with arginine to prepare Arg-MMT, and after observing the adsorption of heavy metal ions, the XRD patterns of Na-MMT and Arg-MMT show that there is ion exchange between Na-MMT and heavy metal ions, as shown in Figure 9, and since the surface of Na-MMT is negatively charged, there is electrostatic adsorption between heavy metal ions and Na-MMT (Chu *et al.*, 2019). The MMT is directly processed to obtain nano-montmorillonite (NMMT). By studying the effect of NMMT on the initial concentration of the solution, it is found that the adsorption sites and cation exchange sites of NMMT are limited, and high-concentration solutions will inevitably reduce the removal rate of heavy metal ions. In addition, under relatively low pH conditions, the removal rate will also decrease, due to the competition between H<sup>+</sup> and Cd(II) for adsorption sites, so surface ion exchange is the main adsorption mechanism, and BET analysis shows the pore size increases after NMMT adsorbs Cd(II), indicating that a certain degree of precipitation and surface adsorption have also occurred (Liu *et al.*, 2017). By analyzing the FTIR spectra before and after the adsorption of the adsorbent, the adsorption mechanism of lignin-MMT to remove heavy metal ions Cu(II) was explored. The absorption peak became weaker after adsorption, and the pH value of the Cu(II) ion solution decreased from 5.0 to 3.2, the results show that the adsorption of Cu(II) by the adsorbent mainly depends on ion exchange (Sun *et al.*, 2019). By analyzing the FTIR of the lignin-MMT (L-MMT) nanocomposite material adsorbing Co(II), it is inferred that the protons on the hydroxyl and carboxyl photo functional groups of L-MMT are replaced by Co(II), which is formed after ion exchange With new chemical bonds, free carboxyl groups are adsorbed and become carboxylates (Zhang *et al.*, 2017b). The metal bond MO (M = Na, Mg, or Fe) existing on the surface of tourmaline is very easy to disintegrate, thereby exposing a large number of metal ions Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> in the aqueous solution. These ions are easily attracted by polar water molecules and leave the crystal. The surface enters the water phase, which generates a large amount of negative potential on the surface of the mineral. It is found that the cation exchange of the TMMs composite

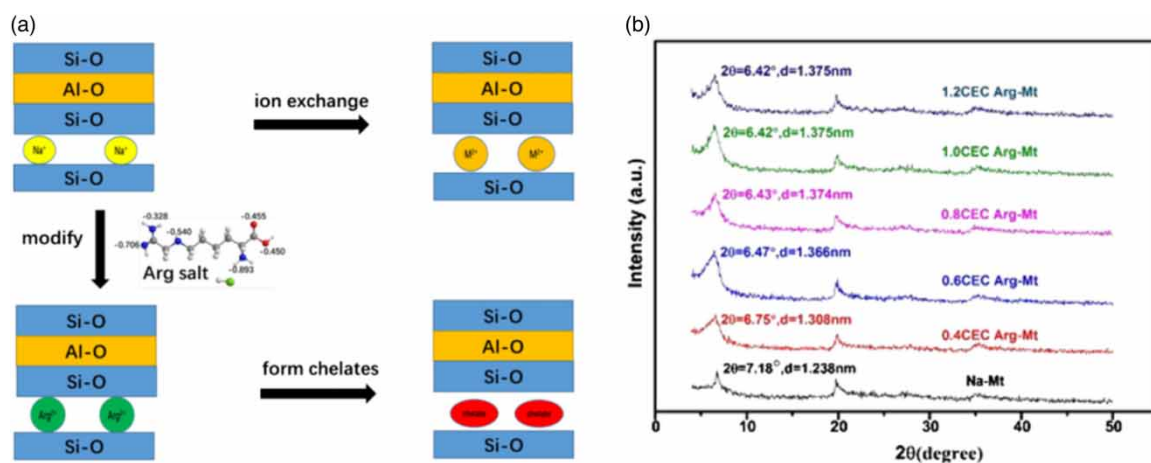


Fig. 9 | Diagrams of (a) Na-MMT and Arg-MMT adsorption mechanism and (b) XRD (Chu *et al.*, 2019). Copyright 2019, Elsevier.

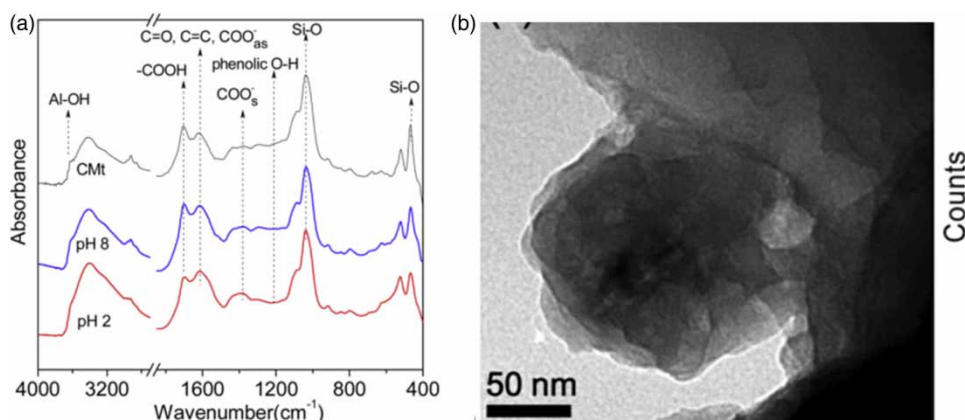
material plays an important role in the immobilization of the metal. In addition, the cations such as  $\text{Na}^+$  and  $\text{Mg}^{2+}$  on the surface of the TMMs will also be complexed by adsorption and exchange of  $\text{Pb}(\text{II})$  to reduce its concentration (Chen *et al.*, 2020).

#### 4.2. Electrostatic adsorption

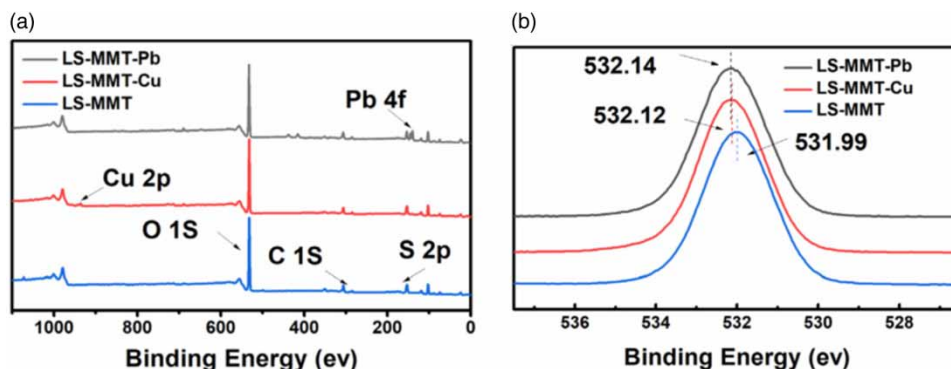
Natural Na-MMT adsorbs heavy metal ions  $\text{Cd}(\text{II})$  under acidic conditions, and its activation energy is 8.51 kJ/mol, indicating that the heavy metal ions studied are physically adsorbed (Yan *et al.*, 2019). The adsorption mechanism of  $\text{Zn}(\text{II})$  on the montmorillonite-loaded biochar composite material studied by SEM-EDS, XRD, FTIR, XPS, and other methods show that the electrostatic interaction and surface complexation dominate (Song *et al.*, 2019).

#### 4.3. Coordination reaction

The chelating agent between the MMT layers can provide sites for coordination and complexation with heavy metal ions, thereby improving the adsorption capacity of heavy metals (sJingDe *et al.*, 2018). Zeta potential analysis confirmed that the surface charge of organically modified MMT changed from negative to positive, indicating that electrostatic attraction is no longer one of the main adsorption methods of STAC-En-MMT. The infrared spectrum analysis after adsorption shows that heavy metal ions form a stable complex with En. A new absorption peak appears, confirming that coordination complexes are dominant in the adsorption of heavy metal ions (Liu *et al.*, 2019). sJingDe *et al.* (2018) modified STAC and organic chelating agent ethylenediamine (En) to prepare a composite material (FMC). The study showed that the adsorption form of  $\text{Zn}(\text{II})$  mainly includes ion exchange and coordination complexation, and the ion exchange capacity is mainly related to the number of exchangeable cations between layers. En loaded on MMT will form a complex with  $\text{Zn}(\text{II})$  (sJingDe *et al.*, 2018). The removal of  $\text{Cr}(\text{VI})$  by CMT includes electrostatic adsorption and also involves the reduction of  $\text{Cr}(\text{VI})$  to  $\text{Cr}(\text{III})$  and the complexation of metal ion  $\text{Cr}(\text{III})$  with surface groups. Infrared spectroscopy analysis is done after adding  $\text{Cr}(\text{VI})$ . The movement of the  $\text{COO}^-$  asymmetric stretching band may be attributed to the complexation between heavy metal ions and carboxylate, and precipitation particles were observed under the transmission electron microscope, indicating that precipitation is also one of the removal mechanisms, as shown in Figure 10 (Yu *et al.*, 2016). The elemental analysis was carried out by X-ray photoelectron spectroscopy (XPS) and it was observed that a new absorption peak appeared on the composite material LS-MMT, as shown in Figure 11, indicating that



**Fig. 10** | Infrared spectrum and transmission electron microscope analysis diagram of CMT under different pH values (Xiaojiang *et al.*, 2019). Copyright 2018, Sustainable Chemistry.



**Fig. 11** | X-ray electron spectroscopy (XPS) analysis of LS-MMT (Ma *et al.*, 2019). Copyright 2019, Elsevier.

lignosulfonate acid sodium salt successfully modified MMT. After adsorbing heavy metal ions Pb(II) and Cu(II), a new absorption peak appeared in the corresponding binding energy region, indicating that heavy metal ions were adsorbed on the surface of the composite material and the binding energy. The slight increase in potential may be due to the fact that after the composite material adsorbs heavy metal ions, a large number of oxygen-containing functional groups chelate the metal ions so that a large number of oxygen atoms tend to provide electrons (Ma *et al.*, 2019). The HPFC/MS-S composite material is used to remove the pollutant Hg(II). When the solution is at a higher pH, the hydroxylated mercury form ( $\text{HgOH}^+$  and  $\text{Hg}(\text{OH})_2$ ) interacts with the active group to produce a neutral complex ( $\text{N-HgOH}$ ). As the adsorption process progresses, more and more hydroxylated mercury forms a chelate and aggregates to the active site of the adsorbent. Under the interference of hydrogen bonds or foreign particles, the aggregates gradually grow up and produce random solid materials. Therefore, the removal of Hg(II) ions involves not only the chelation process that occurs at the adsorbent–solution interface but also the precipitation process on the adsorbent surface (Hrab *et al.*, 2019). When the composite material MEL–CS–MMT removes Fe(III), metal chelation can be achieved through the  $\text{NH}_2$  and OH groups on the CS and the OH groups on the MMT surface. The  $\text{NH}_2$  group and the  $\text{NH}_2$  group on the surface of the MEL are coordinated with Fe(III). The essence is that the heavy metal ion accepts the electron pair of the functional group during the process. In addition, the heavy metal ion Fe(III) may also undergo cation exchange to replace the MMT with cations between layers (Kenawy *et al.*, 2019). The Arg–MMT composite material is mainly due to the fact that Arg enters the interlayer of MMT to increase the interlayer spacing and forms a chelate compound with heavy metal ions, which is fixed between the MMT layers, and finally achieves the effect of removing heavy metal ions (Chu *et al.*, 2019).

## 5. CONCLUSIONS AND PROSPECTS

Based on the performance of modified MMT to remove heavy metal ions, this article summarizes the removal performance and adsorption mechanism of various modified MMTs to remove heavy metal ions.

- The experimental results of pH influence show that in the process of modified MMT adsorbing heavy metal ions in water, most of the adsorbents show excellent removal performance under acidic conditions. In the experiments, for different modified MMT adsorption of different concentrations of heavy metal ions, the suitable initial pH is different, and different pH values also lead to different adsorption mechanisms of adsorbents.



- After proper modification, the adsorption effect will be significantly improved compared to natural MMT. Multidisciplinary approaches involving biotechnology and chemistry have opened up ways to develop adsorption materials, which are very useful to reduce the toxicity of heavy metals.
- The main adsorption mechanism of pickling and heat treatment-modified MMT to heavy metals is ion exchange; the adsorption mechanism of inorganic-modified MMT to heavy metals includes ion exchange and electrostatic adsorption; the adsorption mechanisms of organic-modified MMT for heavy metals are ion exchange and ligand complexation reaction.

At present, many achievements have been made in the research of removing heavy metals based on modified MMT, but there are still a series of problems. The main reason is that the adsorption effect of modified MMT and the reaction conditions of modified MMT need to be further optimized. Seeking a modified adsorbent with good adsorption performance, low preparation cost and simple preparation steps are the key to its application in practical engineering. The adsorption process can be combined with advanced oxidation to improve the efficiency of the adsorbent. The adsorption mechanism of the adsorbent is different at different pH values, and the adsorption mechanism of MMT modified by different methods should be further studied, and then the synthesis could be efficient and can be applied to practical engineering. Thus, the obtained adsorbent can be used to treat industrial wastewater containing many pollutants. Based on the experiment, the actual industrial wastewater is simulated to explore the adsorption performance of heavy metal ions under the influence of multiple pollutants.

#### AUTHORS CONTRIBUTIONS

Y.S. and S.Z. did the investigation; wrote, prepared, reviewed, and edited the original draft. S.Z., X.W., and C.F. were involved in data curation. All authors have read and agreed to the published version of the manuscript.

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#### DATA AVAILABILITY STATEMENT

All relevant data are available from an online repository or repositories.

#### CONFLICT OF INTEREST

The authors declare there is no conflict.

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