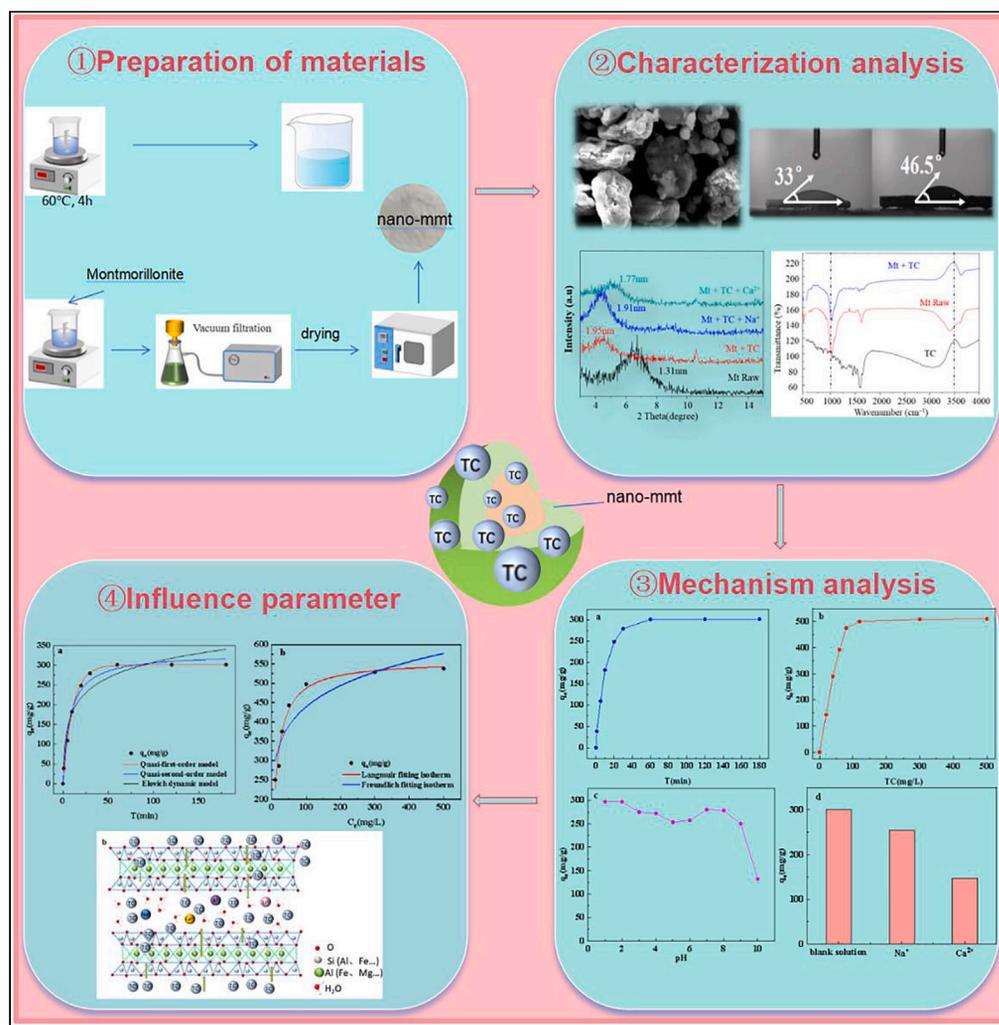


Article

Nano-clay montmorillonite removes tetracycline in water: Factors and adsorption mechanism in aquatic environments



Yan Shi, Xin Wang,
Changping Feng,
Shipeng Yang

syshiyang@126.com

Highlights
Nano-montmorillonite was successfully prepared

The factors affecting the adsorption of antibiotics by montmorillonite were analyzed

The adsorption mechanism of montmorillonite was revealed

Montmorillonite can be used as an efficient adsorbent for TC wastewater



Article

Nano-clay montmorillonite removes tetracycline in water: Factors and adsorption mechanism in aquatic environments

Yan Shi,^{1,2,3,*} Xin Wang,¹ Changping Feng,¹ and Shipeng Yang¹

SUMMARY

In response to escalating environmental concerns surrounding antibiotic pollution, the utilization of calcium-montmorillonite minerals for tetracycline wastewater treatment is gaining prominence. This study systematically analyzed the physicochemical properties of calcium-montmorillonite through scanning electron microscope, contact angle analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. It explored the adsorption efficacy and mechanisms for tetracycline removal, considering factors like initial pH, adsorption duration, concentration, and co-cations (Na^+ and Ca^{2+}). Under optimized conditions, achieving over 90% tetracycline removal with a maximum adsorption capacity of 526 mg/g, the study revealed competitive adsorption sites for coexisting cations. The Langmuir model best described the monolayer adsorption process, while kinetic studies favored the pseudo-first-order model. This research offers comprehensive insights into tetracycline adsorption on calcium-montmorillonite, emphasizing its potential as an efficient, cost-effective adsorbent for pharmaceutical wastewater treatment.

INTRODUCTION

Tetracycline drugs have a wide range of applications in animal and in the aquaculture industry, which is due to factors such as their low cost, broad spectrum, and high antimicrobial activity.¹ The dosage of tetracycline is large, but its absorption and utilization rates are low in animals,² which causes 50%–80% of tetracycline drugs to enter the natural environment as antibiotic pollutants without being metabolized.³ A large number of antibiotics in the environment will lead to an increase in antibiotic-resistant bacteria. Tetracycline drugs in soil and water will also enter the human body through the food chain,^{4,5} which ultimately poses a risk that endangers human health. Figure 1 shows the molecular formula of tetracycline.

Montmorillonite is the main mineral composition of inorganic non-metallic mineral bentonite. According to the types of exchangeable cations, bentonite can be divided into four categories: sodium-based, calcium-based, Mg-based, and Al (hydrogen)-based bentonite.⁶ The general structure of montmorillonite is ${}^{\text{IV}}(\text{Si}_4){}^{\text{VI}}(\text{Al}_{2-y}\text{Mg}_y)\text{O}_{10}(\text{OH})_2 \cdot y\text{M} + n\text{H}_2\text{O}$ (M^+ is interlayer exchangeable cation).⁷ Its main components are Si, Al, Fe, and Mg oxides. Montmorillonite minerals belong to 2:1 type of Al-Mg layered silicate minerals containing H_2O . Two layers of Si-O tetrahedron and one layer of Al-(O, OH) octahedron make up the structural unit, with adjacent structural layers frequently forming an interlayer domain containing hydration cations,^{8,9} belonging to the monoclinic system. Figure 2 shows the structural formula of montmorillonite. The Si^{4+} in the silica tetrahedron can be replaced by Al^{3+} and Fe^{3+} , and the Al^{3+} in the alumina octahedron can be replaced by low-valent cations such as Mg^{2+} and Fe^{2+} , which makes the crystal structure of montmorillonite negatively charged. In order to achieve electrical charge balance, montmorillonite cells adsorb exchangeable cations. They are located between the unit layers, so their interlayer domains have good ion exchange properties and adsorption characteristics.^{10,11} Montmorillonite also has nano or micron particle size and large specific surface area, and its end face often contains a large number of hydroxyl groups (such as silanol group, Al/Mg/Fe hydroxy).^{12,13} In addition, there are Brønsted acid (B acid) and Lewis acid (L acid) on the surface and edge of montmorillonite.¹⁴ These structural characteristics of montmorillonite determine that it has strong surface/interface reactivity, and its structure and properties are easy to control.¹⁴

Adsorption uses porous materials with a large specific surface area, known as adsorbents, to treat pollutants in wastewater.^{15,16} Adsorbent properties are what determine the method of absorbance. Adsorption can be divided into three basic types: exchange adsorption, physical adsorption, and chemical adsorption. Adsorption occurs when the solute gathers on the surface of the adsorbent and replaces the charged ions on the surface of the adsorbent under the action of electrostatic attraction.¹⁷ Physical adsorption is due to the van der Waals force between solute and adsorbent. The solutes adsorbed physically have no fixed position on the adsorbent surface.¹⁸ Chemical adsorption refers to the process of chemical reaction between a solute and an adsorbent to form chemical bonds and surface complexes.¹⁸ Adsorption can occur by one or more of these methods simultaneously.

¹School of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450046, China

²Collaborative Innovation Center for Efficient Utilization of Water Resources, Zhengzhou 450046, China

³Lead contact

*Correspondence: syshiyang@126.com

<https://doi.org/10.1016/j.isci.2024.108952>



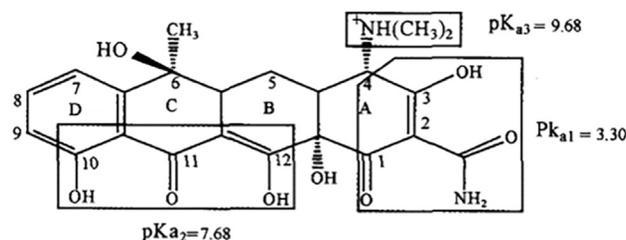


Figure 1. Structural formula of tetracycline

Montmorillonite is widely distributed in nature with rich reserves and low prices. It is widely used to prepare multi-functional environmental materials for the adsorption and removal of various pollutants in sewage. Montmorillonite has good adsorption capacity for heavy metal, radionuclide,^{22–24} phosphate,^{25–27} and other ions.^{28–30} However, due to the existence of strong polar groups on the surface and end face of its structural lamella, montmorillonite generally shows strong hydrophilicity and hydrophobicity, which makes its adsorption performance for weak polar and non-polar organic substances poor, limiting its application scope.¹⁴

In order to expand the scope and depth of the application of montmorillonite, the adsorption experiment of tetracycline with calcium-montmorillonite was put forward to study its adsorption performance.¹ At the same time, the effects of initial pH, adsorption duration, initial concentration, and co-cations (Na^+ , Ca^{2+}) electrolytes on tetracycline adsorption were investigated.³¹ Scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), contact angle, and other characterization methods were used to study the structural characteristics of montmorillonite, and the adsorption mechanism was analyzed in combination with the structural characteristics and adsorption performance to provide a theoretical basis for montmorillonite to adsorb antibiotic organics.

Experimental instruments and materials

The instruments used in the experiment include constant-temperature oscillator, high-speed centrifuge, ultraviolet-visible spectrophotometer, SEM, infrared spectrometer, X-ray powder diffractometer, and contact angle measuring instrument.

Tetracycline; molecular formula: $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$; calcium-montmorillonite, the place of origin is Ningcheng, Inner Mongolia, with a cation exchange capacity (CEC) of 97.9 mmol/100 g (CEC determined according to the national standard method), as detailed in Table 1; hydrochloric acid (HCl); distilled water; calcium chloride (CaCl_2); sodium hydroxide (NaOH); and sodium chloride (NaCl).

Preparation of nano-montmorillonite

Referring to the experimental method of Pi Zhenbang, the preparation method of nano-montmorillonite is as follows. (1) Sequentially add the following components to the container: 8.6 g of butyl acetic acid, 25 mL of distilled water, 22 mL of hydrochloric acid, and 32 mL of anhydrous ethanol. Maintain temperature at 60 °C at atmospheric pressure and stir the reaction for 4 h to obtain a gel. (2) Add 5 g of montmorillonite powder to the gel obtained in the previous step. Maintain the temperature at 60 °C at atmospheric pressure and continue stirring for 4 h. Then, proceed with filtration, separation, washing, and finally drying to obtain the end product.

Adsorption experiment

A certain amount of montmorillonite was weighed into a conical flask, and 100 mL of simulated wastewater containing tetracycline was added. The conical bottle was placed in a 25 °C constant-temperature oscillator to oscillate (180 r/min) away from light. After oscillating for a period of time, appropriate amount of supernatant was taken and the concentration of tetracycline in adsorbed wastewater was determined by ultraviolet spectrophotometer.

- (1) The impact of different adsorption times on adsorption efficiency
0.03 g of calcium-montmorillonite was added to a 50 mL tetracycline solution with an initial concentration of 200 mg/L and a pH of 4. The experiment was conducted following the method described earlier. Samples were collected at intervals of 0, 1, 5, 10, 30, 60, 120, and 180 min, and their concentrations were analyzed.
- (2) The impact of different initial tetracycline concentrations on adsorption efficiency
0.03 g of calcium-montmorillonite was added to a 50 mL tetracycline solution with varying initial concentrations of 20, 40, 60, 80, 120, 300, and 500 mg/L, all at a pH of 4. The experiment was conducted following the method described earlier, and the results were analyzed.
- (3) The impact of different initial pH values on adsorption efficiency
0.03 g of calcium-montmorillonite was added to a 50 mL tetracycline solution with an initial concentration of 200 mg/L. The pH was adjusted to different levels, including pH 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The experiment was conducted following the method described earlier, and the results were analyzed.

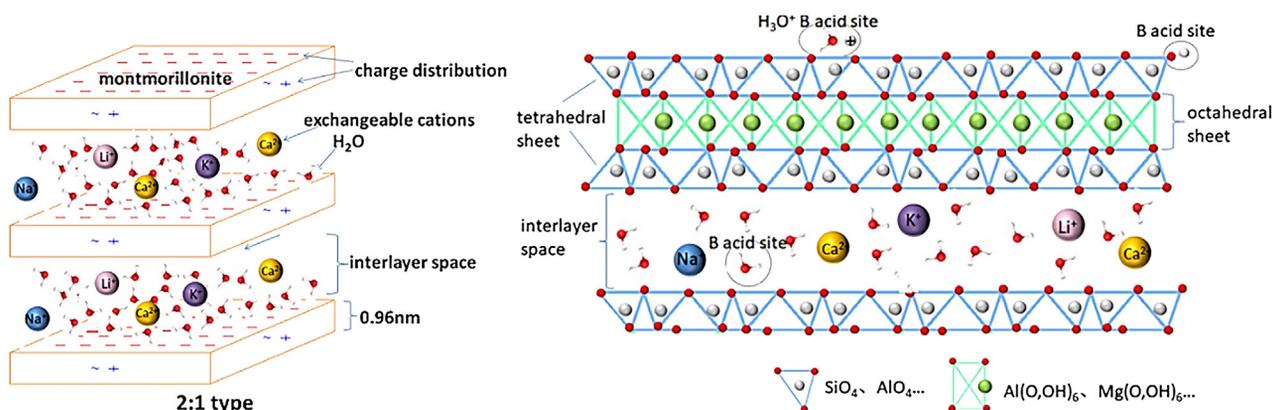


Figure 2. Schematic diagram of montmorillonite layered structure

(4) The impact of different electrolytes on adsorption efficiency

0.03 g of calcium-montmorillonite was added to a 50 mL tetracycline solution with an initial concentration of 200 mg/L and a pH of 1. Solutions containing Na^+ and Ca^{2+} at a concentration of 0.1 mol/L were prepared separately and added to the solution. A blank solution (without the addition of any cations) was also prepared. The experiment was conducted following the method described earlier, and the results were analyzed.

Characterization methods for adsorbents

The material was characterized using a SEM (JSM-IT300, Japan) with a scanning voltage of 20.0 kV. Contact angle analysis was performed using a contact angle measurement instrument (ZH10692, China). XRD analysis of the material before and after modification was carried out using an X-ray diffractometer (RIGAKU Ultima IV, Japan) with a cobalt target, a radiation voltage of 40 kV, and a current of 30 mA. The diffraction spectrum was collected in the angular range of 5° – 80° , with a scanning speed of $10^\circ/\text{min}$. FTIR spectroscopy analysis of the material was conducted using an infrared spectrometer (SHIMADZU IR Tracer 100, Japan). The samples were prepared with potassium bromide (KBr) microspheres, and the wavenumber range analyzed was 400 – $4,000\text{ cm}^{-1}$. The surface area, pore volume, and pore size of the material were determined using a Brunauer-Emmett-Teller (BET) surface area analyzer (ASAP 2020HD88, USA) at a measurement temperature of 77 K.

Adsorption model

Adsorption dynamic model

The quasi-first-order kinetic equation uses adsorption capacity to describe the adsorption rate, which can explain the adsorption kinetic process of various adsorbents. The equation is expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (\text{Equation 1})$$

where q_t is the adsorption capacity at t , mg/g; q_e is the equilibrium adsorption capacity, mg/g; and k_1 is the rate constant for adsorption reaction, min^{-1} ; The pseudo-second-order kinetic equation is suitable for describing the whole adsorption process, and its equation can be expressed as

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

where q_t is the adsorption capacity at t , mg/g; q_e is the equilibrium adsorption capacity, mg/g; and k_2 is the rate constant for second-order reaction, $\text{g}/(\text{mg} \cdot \text{min})$. Elovich dynamic equation is suitable for describing the whole adsorption process, and its equation can be expressed as

$$q_t = a + k \ln t \quad (\text{Equation 3})$$

here q_t is the adsorption capacity at t , mg/g; k is the adsorption rate constant, $\text{mg}/(\text{g} \cdot \text{min})$; and a is a constant.

Isothermal adsorption model

The isothermal adsorption model of Langmuir and Freundlich equation was used to study the adsorption behavior of montmorillonite on tetracycline.^{32–34}

Table 1. CEC of montmorillonite from Ningcheng, Inner Mongolia

Material	CEC (mmol/100g)	Ca ²⁺ (100 g) tendency	Mg ²⁺ (100 g) tendency
Natural montmorillonite	97.9	44.2	3.6

CEC is the cation exchange capacity.

The Langmuir isothermal model assumes that the monolayer covers the surface of the adsorbent, and the adsorbents have the same force on the solid surface and do not interact with each other.^{35–37} Its expression is given as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot k_f} \quad (\text{Equation 4})$$

where q_e is the adsorption capacity at equilibrium reaction, mg/g; q_m is the maximum adsorption capacity, mg/g; C_e is the concentration of pollutants in equilibrium solution, mg/L; and k_f is the adsorption constant.

The Freundlich isothermal model is based on multi-layer adsorption on heterogeneous surface, and its expression is as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f \quad (\text{Equation 5})$$

where q_e is the adsorption capacity of unit mass adsorbent for pollutants, mg/g; C_e is the concentration of pollutants in equilibrium solution, mg/L; k_f is the adsorption constant; and $\frac{1}{n}$ is the adsorption nonlinearity parameter.

RESULTS AND DISCUSSION

Influence of various factors on the adsorption effect of tetracycline

The effect of adsorption duration on adsorption of tetracycline by calcium-montmorillonite

Figure 3A presented the effect of duration on adsorption performance. The adsorption efficiency of the tetracycline solution showed an overall upward trend with increased duration. The adsorption tended to be stable after 60 min and indicated that the adsorption equilibrium time was 60 min.

The effect of initial concentration of solution on adsorption of tetracycline by calcium-montmorillonite

As shown in the Figure 3B, the system's adsorption amount gradually increased to a steady state as the initial concentration of tetracycline increased. At this time, the maximum adsorption capacity of tetracycline was 500 mg/g and the equilibrium concentration was 120 mg/L. The adsorption capacity of the system did not change significantly when the initial concentration of tetracycline was further increased.

The effect of different values of pH on adsorption of tetracycline by calcium-montmorillonite

As shown in Figure 3C, the removal effect of calcium-montmorillonite on tetracycline was better in acid conditions and worse in alkaline conditions. When pH = 1, the adsorption capacity of tetracycline adsorbed by calcium-montmorillonite was 296.7 mg/g. When pH = 10, the adsorption capacity of tetracycline was only 132.3 mg/g. This result is the same as that of Zou et al.³⁸

The effect of different cation types of electrolyte on adsorption of tetracycline by calcium-montmorillonite

The addition of different cation types of electrolytes in the adsorption process had a great influence on the adsorption of tetracycline by calcium-montmorillonite. When Na⁺ and Ca²⁺ electrolyte ions were added, the maximum adsorption capacity of tetracycline was 254.1 mg/g and 147.3 mg/g, respectively. It showed that the addition of cations made the cations in the solution compete with tetracycline, thus reducing the adsorption capacity of the target adsorbate. This was consistent with the findings of Zou et al.³⁸ Figure 3D illustrated that the effect of Ca²⁺ on the adsorption of tetracycline by calcium-montmorillonite is much greater than that of Na⁺. It can be inferred that the higher the valence of cations the stronger the ability to compete for the adsorption sites of montmorillonite minerals.

Adsorbent characterization

- (1) The particle size of sodium calcium-montmorillonite is about 10 μm. It can be seen from Figure 4A that the particles are gathered by some small layers. The contact angle of calcium-montmorillonite before and after adsorption of tetracycline changed significantly. As shown in Figure 4B, the contact angle of calcium-montmorillonite without adsorption of tetracycline was 33°, while the contact angle became 46.5° after adsorption of tetracycline. It can be inferred that calcium-montmorillonite changed from hydrophilicity before adsorption of tetracycline to hydrophobicity after adsorption of tetracycline.³⁹ Comparing with the XRD patterns of calcium-montmorillonite at different initial concentrations in Figure 4C, it can be seen that the peak shifted to

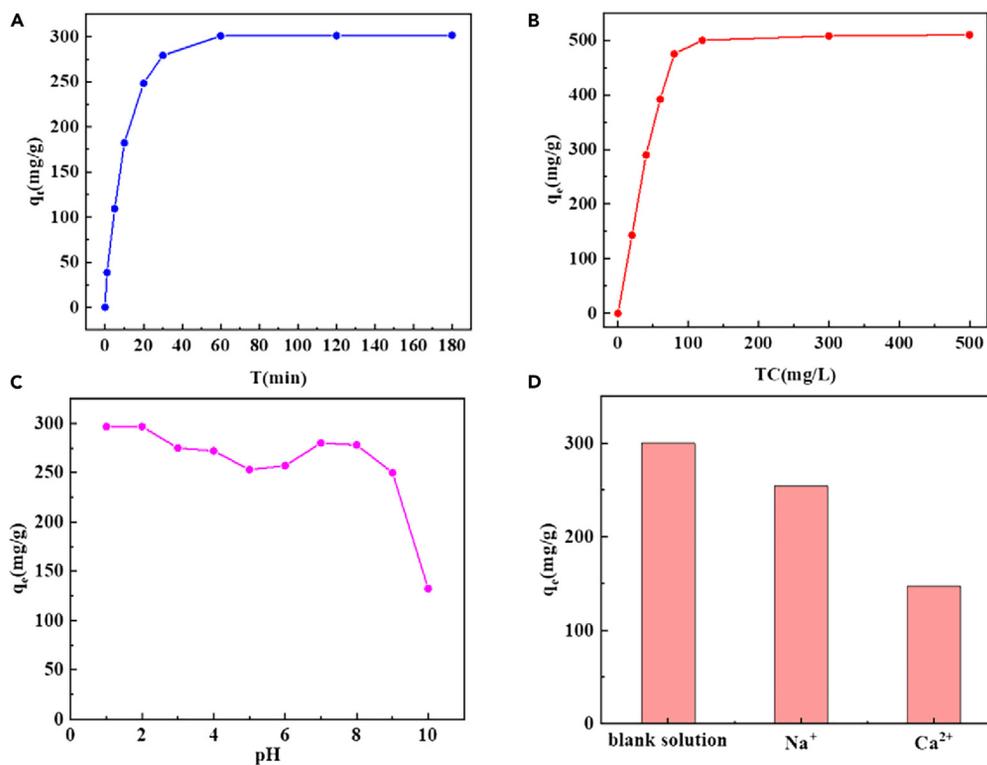


Figure 3. Influence of various factors on tetracycline adsorption

(A) Change of adsorption capacity with time.

(B) Variation of adsorption capacity with initial concentration of tetracycline (TC).

(C) Change of adsorption capacity with initial pH.

(D) Effect of different cation types of electrolyte on adsorption of tetracycline by montmorillonite.

a small angle with the increase of solution concentration, indicating that the interlayer spacing of calcium-montmorillonite had changed. There was a strong absorption band near the middle frequency range of $1,030\text{ cm}^{-1}$ in the infrared spectrum of calcium-montmorillonite, which was caused by the antisymmetric stretching vibration of Si-O-Si of calcium-montmorillonite. It can be seen from Figure 4D that the interlayer spacing of calcium-montmorillonite increased with the addition of tetracycline, but the interlayer spacing of calcium-montmorillonite after the addition of cations was smaller than that without cationic electrolyte, especially when Ca^{2+} electrolyte was added, showing that the cationic electrolyte formed a competitive relationship with tetracycline and inserted into the layers of calcium-montmorillonite. As shown in Figure 4E, combined with the infrared spectrum, tetracycline molecule had been adsorbed by calcium-montmorillonite. The results of the determination of the specific surface area and pore structure of nanoscale montmorillonite are as follows: BET specific surface area is $247\text{ m}^2/\text{g}$; total pore volume is $9.84\text{ cm}^3/\text{g}$; and average particle size is 364 nm . This indicates that nanoscale montmorillonite particles have a relatively substantial specific surface area and a significant pore structure, making them suitable for use as an efficient adsorbent for adsorbing tetracycline.

The recycling and utilization of nano-montmorillonite

After the adsorption of tetracycline by nano-montmorillonite, the recovery and reuse of the adsorbent typically involve several methods, including physical methods (precipitation, filtration), chemical methods (acid-base washing, desorption), thermal regeneration (high-temperature treatment), wastewater treatment, and reuse (wastewater treatment, soil improvement). Many scholars have conducted extensive research on this topic. Tang et al. treated the products of magnetic montmorillonite adsorbed with tetracycline by placing them in a solution of 50 mg/L potassium persulfate ($K_2S_2O_8$). Oscillation desorption was performed for 30 min at room temperature, followed by solid-liquid separation under the conditions of an applied magnetic field for the recovery of montmorillonite. The results indicated that the material could be reused for up to 5 cycles.⁴⁰ Maged et al. utilized 0.1 M NaOH as an eluent for regeneration studies on thermally activated montmorillonite adsorbed with tetracycline, demonstrating that the material could be reused for 5 cycles.⁴¹ Zhang employed high-temperature calcination for the recovery of magnetic montmorillonite after adsorption of tetracycline. The study showed that, after three cycles of calcination regeneration, the regeneration rate remained above 80%.⁴²

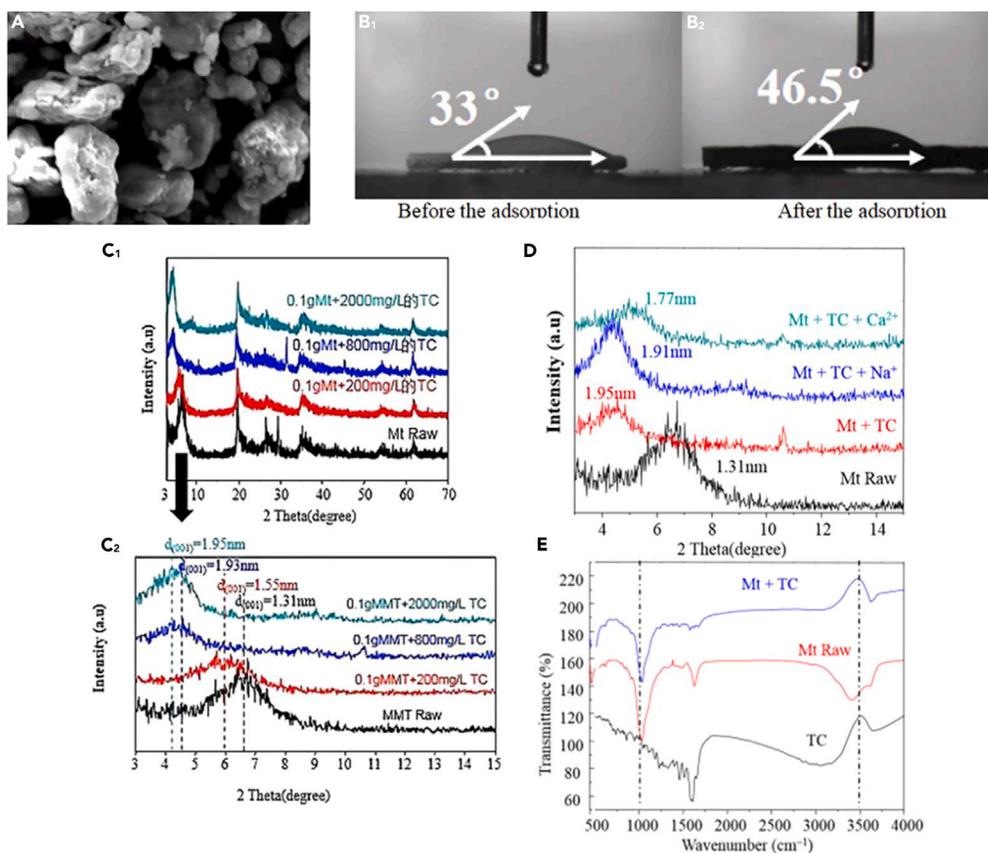


Figure 4. Characterization of nano-montmorillonite

(A) SEM image of montmorillonite (Measurement conditions: JSM-IT300 scanning electron microscope was used, and the scanning voltage was 20.0 kV).

(B₁ and B₂) Change of contact angle of montmorillonite before and after adsorption of tetracycline(TC).

(C₁ and C₂) XRD of montmorillonite at different initial concentrations of tetracycline(TC).

(D) XRD patterns of montmorillonite added with different electrolyte cation types.

(E) FTIR analysis of montmorillonite after adsorption of tetracycline(TC).

Adsorption mechanism

Adsorption kinetics analysis

The pseudo-first and second-order kinetics fitting curves of calcium-montmorillonite adsorption tetracycline were shown in Figure 5A. As can be seen from Table 2, the R² value of the pseudo-first-order kinetic model is 0.986, which is larger than that of the second-order kinetic model and Elovich model. Therefore, the fitting accuracy of the quasi-first-order kinetic equation was better than that of the quasi second-order kinetic equation. The pseudo-first-order kinetic equation's reaction rate k was 0.291 g/(mg·min). The pseudo-first-order kinetic equation showed that physical adsorption is the main interaction between adsorbent and adsorbate. This result is the same as that of Zhang et al.⁴²

Adsorption isotherm analysis

The Langmuir and Freundlich fitting isotherm fitting curves for the adsorption of tetracycline by calcium-montmorillonite are shown in Figure 5B. It can be seen from Table 3 that the linear correlation coefficient fitted by the Langmuir isotherm equation was 0.974, which was higher than that fitted by the Freundlich isotherm equation. This was indicative that the adsorption process was more consistent with the uniform adsorption of the monolayer described by the Langmuir equation. The maximum adsorption capacity calculated by Langmuir isotherm adsorption model was 558.184 mg/g. This value was consistent with the experimental data. The 1/n of the Freundlich equation was 0.170, meaning that the adsorption index n was greater than 1, indicating that the adsorption nonlinearity of calcium-montmorillonite on tetracycline was significant and that there were different adsorption sites for calcium-montmorillonite adsorption.⁴³

Mechanism analysis of reaction system

Montmorillonite belongs to monoclinic system, and its crystal structure is characterized by the combination of two layers of silicon oxide tetrahedron chips and one layer of Al oxide octahedron chip between them to form a crystal layer. The two structural unit layers are combined by

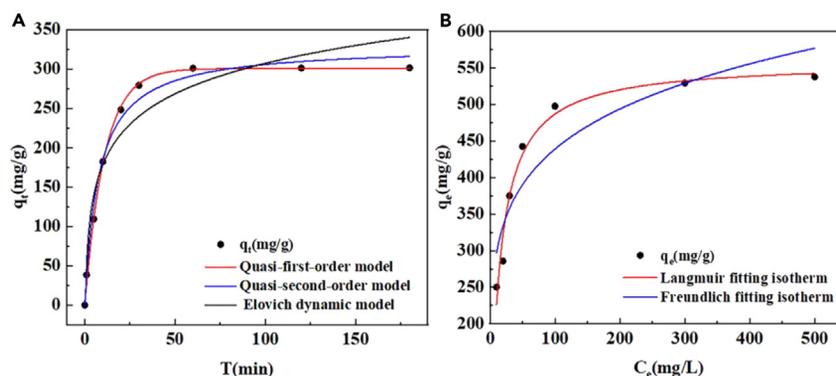


Figure 5. Kinetic fitting and isotherm fitting

(A) Kinetic fitting curve.

(B) Langmuir and Freundlich fitting isotherm.

molecular force, and the structure is relatively loose, which will cause relative movement and expansion between the lower layers under the action of external force or polar water molecules. Al ions in Al-O octahedron can be replaced by Mg, iron, zinc, and other ions.^{44–46} The replacement rates can reach 20%–30%. Therefore, montmorillonite minerals have the ability to adsorb cations and polar organic molecules. Tetracycline has different ionization functional groups. As shown in Figure 6A, the charge number of tetracycline molecules was also different when the pH value of the solution was different. Tetracycline exists in four forms in aqueous solution.^{47–50} When pH is less than 3.3, it mainly exists in the form of monovalent cation. When pH is between 3.3 and 7.7, it mainly exists in the form of amphoteric ions. When pH is greater than 7.7, tetracycline mainly exists in the form of univalent anion or bivalent anion. When pH is greater than 9.3, it mainly exists in molecular form. Montmorillonite is an interlayer negatively charged mineral. Under acidic conditions, tetracycline existed in the solution in the form of cation. Due to the electrostatic attraction, it was easy for tetracycline to enter the interlayer of montmorillonite to replace its interlayer cation and increase the interlayer spacing. Under alkaline conditions, tetracycline existed in molecular form or negatively charged form, so ion exchange is not easy with montmorillonite. Moreover, tetracycline was an organic matter, which changed the hydrophilicity and hydrophobicity of montmorillonite after adsorbing tetracycline. Figure 6B showed the adsorption mechanism of montmorillonite on tetracycline.

Conclusion

- (1) Nano-montmorillonite demonstrates remarkable adsorption efficiency for tetracycline. Optimal reaction conditions (initial tetracycline concentration of 120 mg/L, initial pH of 1, adsorption time of 60 min, and an optimal dosage of 0.03 g/L calcium-based montmorillonite) can achieve a tetracycline removal rate exceeding 90%, with a maximum adsorption capacity of 526 mg/g.
- (2) The adsorption process is best described by the Langmuir equation, signifying homogeneous adsorption involving a single molecular layer. Tetracycline adsorption onto montmorillonite occurs as a monolayer physical adsorption. The results reveal that tetracycline can intercalate within the interlayer of montmorillonite, leading to a significant alteration in the contact angle of montmorillonite, transitioning from hydrophilic to hydrophobic.
- (3) Nano-montmorillonite emerges as an efficient adsorbent for tetracycline wastewater treatment, offering promising prospects for practical applications.

Limitations of the study

The adsorption performance is significantly influenced by environmental factors, such as water pH and temperature. This variability makes it challenging to maintain consistent removal efficiency for tetracycline under different water quality conditions, restricting its applicability in diverse environments.

Table 2. Related parameters of the kinetic model of TC adsorption by montmorillonite

Parameter	k	q _e	R ²
Pseudo-first-order model	0.091	300.567	0.998
Pseudo-second-order model	0.071	329.733	0.989
parameter	k	a	R ²
Elovich dynamic model	55.913	55.913	0.849

k is adsorption rate constant, q_e is equilibrium adsorption capacity, R² is correlation coefficient, a is constant.

Table 3. Relevant parameters of Langmuir and Freundlich models for TC adsorption by montmorillonite

	q_m (mg/g)	k_f (L/mg)	R^2
Langmuir model	558.184	0.068	0.974
	k_f (mg/g)	1/n	R^2
Freundlich model	200.706	0.170	0.846

q_m is maximum adsorption capacity, k is adsorption rate constant, R^2 is correlation coefficient, a is constant, $1/n$ is adsorption nonlinearity parameter.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
 - Lead contact
 - Materials availability
 - Data and code availability
- EXPERIMENTAL MODEL AND STUDY PARTICIPANT DETAILS
- METHOD DETAILS
 - Materials
 - Preparation of nano montmorillonite
 - Scanning electron microscopy (SEM) results and analysis
 - Characterization and analysis of contact angle
 - X-Ray diffraction (XRD) results and analysis
 - Fourier infrared spectroscopy (FT-IR) results and analysis
- QUANTIFICATION AND STATISTICAL ANALYSIS

ACKNOWLEDGMENTS

The research was partially supported by Training Plan for Young Backbone Teachers in Colleges and Universities in Henan Province (2019GGJS098 and 2020GGJS098) and Master Innovation ability improvement project of North China University of Water Resources and Electric Power.

AUTHOR CONTRIBUTIONS

Y.S. designed the research; X.W., C.F., and S.Y. carried out operation of specific experiments; Y.S. and X.W. wrote and revised the paper; X.W. and C.F. analyzed the data.

DECLARATION OF INTERESTS

The authors declare no competing interests.

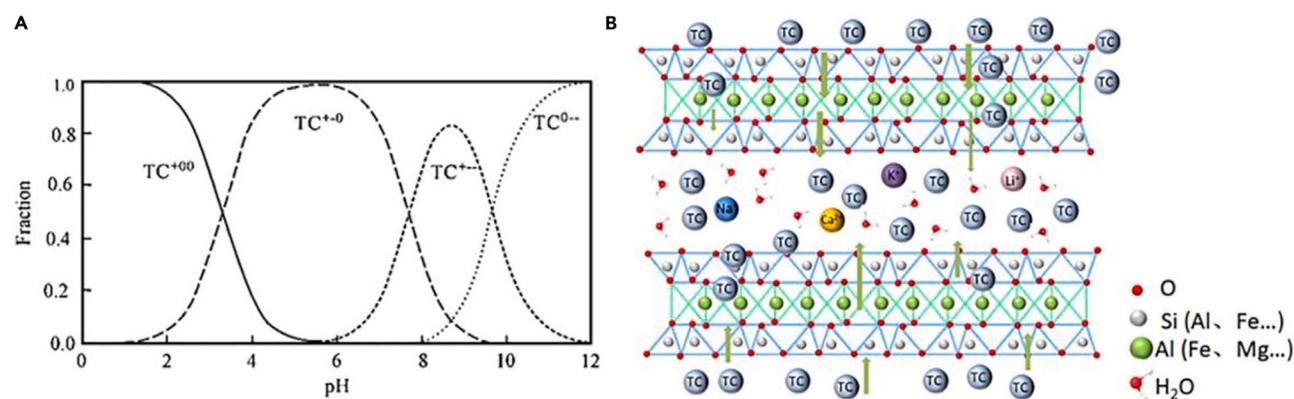


Figure 6. Adsorption mechanism of tetracycline by nano-montmorillonite

(A) The different existence form of tetracycline hydrochloride under the condition of different medium pH.

(B) Adsorption mechanism of calcium-montmorillonite to tetracycline under acidic conditions.

Received: June 27, 2023

Revised: January 1, 2024

Accepted: January 15, 2024

Published: January 17, 2024

REFERENCES

- Ren, S., Wang, S., Liu, Y., Wang, Y., Gao, F., and Dai, Y. (2023). A review on current pollution and removal methods of tetracycline in soil. *Separ. Sci. Technol.* **58**, 2578–2602.
- Liu, M., Lv, G., Mei, L., Wang, X., Xing, X., and Liao, L. (2014). Degradation of Tetracycline by Birnessite under Microwave Irradiation. *Adv. Mater. Sci. Eng.* **2014**.
- Bound, J., and Voulvoulis, N. (2004). Pharmaceuticals in the aquatic environment: a comparison of risk assessment strategies. *Chemosphere* **56**, 1143–1155.
- Batt, A.L., Bruce, I.B., and Aga, D.S. (2006). Evaluating the vulnerability of surface waters to antibiotic contamination from varying wastewater treatment plant discharges. *Environ. Pollut.* **142**, 295–302.
- Jiang, W., Chang, P., Wang, Y., Tsai, Y., Jean, J., and Li, Z. (2014). Sorption and desorption of tetracycline on layered manganese dioxide birnessite. *Environ. Sci. Technol.* **9**.
- Li, G., Ma, H., Wang, H., Wang, H., Zhang, J., and Liu, M. (2011). Modal analysis of montmorillonite in bentonites using phase mixing equation: A comparative study. *Earth Sci. Front.* **18**, 216–221.
- Bergaya, F., and Lagaly, G. (2013). General introduction: clays, clay minerals, and clay science. In *Developments in clay science*, **5** (Elsevier), pp. 1–19.
- Schmidt, S., Katti, D., Ghosh, P., and Katti, K. (2005). Evolution of mechanical response of sodium montmorillonite interlayer with increasing hydration by molecular dynamics. *Langmuir* **21**, 8064–8076.
- Tambach, T., Bolhuis, P., Hensen, E., and Smit, B. (2006). Hysteresis in clay swelling induced by hydrogen bonding: Accurate prediction of swelling states. *Langmuir* **22**, 1223–1234.
- Boek, E., Coveney, P., and Skipper, N. (1995). Molecular modeling of clay hydration: A study of hysteresis loops in the swelling curves of sodium montmorillonites. *Langmuir* **11**, 4629–4631.
- Mignon, P., Ugliengo, P., Sodupen, M., and Hernandez, E. (2010). Ab Initio Molecular Dynamics Study of the Hydration of Li⁺, Na⁺ and K⁺ in a Montmorillonite Model. Influence of Isomorphic Substitution. *Phys. Chem. Chem. Phys.* **12**, 688–697.
- Uddin, F. (2018). Montmorillonite: An Introduction to Properties and Utilization (IntechOpen).
- Zhu, R., Zeng, C., Zhou, Q., Zhu, J., and He, H. (2017). Recent Advances on the Modified Montmorillonite and Their Applications for Contaminant Removal. *Bull. China Soc. Mineral Petrol. Geochem.* **36**, 697–705.
- Qing, Y., Su, X., Wang, Y., Zhou, Q., Wen, K., Ma, L., Chen, Q., and Zhu, J. (2020). Research Progress in Construction of Montmorillonite Environmental Mineral Materials. *Mater. Rep.* **34**, 19018–19026.
- Wei, H., Na, L., Dong, S., Chun, H., Chun, Z., and Chuan, Y. (2013). Adsorption of proteins and nucleic acids on clay minerals and their interactions: A review. *Appl. Clay Sci.* **80**, 443–452.
- Feng, H., Li, W., Yang, Z., Ruan, X., and Xing, Y. (2006). Characteristics of adsorption and desorption of phosphate by sediments in the Suzhou River, East China. *Earth Sci. Front.* **13**, 113–118.
- Ahmadi, S., Akbari, N., Shiri-Yekta, Z., Mashhadizadeh, M., and Pourmatin, A. (2014). Adsorption of strontium ions from aqueous solution using hydrous, amorphous MnO₂-ZrO₂ composite: a new inorganic ion exchanger. *J. Radioanal. Nucl. Chem.* **299**, 1701–1707.
- Liu, D., and Wang, J. (1999). Physical adsorption and chemical adsorption. *J. Shandong Inst. Light Ind. (Nat. Sci. Ed.)* **02**, 24–27.
- Liu, L., Zhang, C., Jiang, W., Li, X., Dai, Y., and Jia, H. (2021). Understanding the sorption behaviors of heavy metal ions in the interlayer and nanopore of montmorillonite: A molecular dynamics study. *J. Hazard Mater.* **416**, 125976.
- Moreno-Sader, K., Alvaro, G.-P., Realpe, A., María, A.-M., and Soares, J.B.P. (2019). Removal of heavy metal water pollutants (Co²⁺ and Ni²⁺) using polyacrylamide/sodium montmorillonite (PAM/Na-MMT) nanocomposites. *ACS Omega* **4**, 10834–10844.
- Shi, Y., Zhong, S., Wang, X., and Feng, C. (2022). A review of the removal of heavy metal ions in wastewater by modified montmorillonite. *Water Pol.* **24**, 1590–1609.
- Yu, S., Me, H., Chen, X., Tan, X., Ahmad, B., Alsaedi, A., Hayat, T., and Wang, X. (2015). Impact of environmental conditions on the sorption behavior of radionuclide ⁹⁰Sr (II) on Na-montmorillonite. *J. Mol. Liq.* **203**, 39–46.
- Huber, F.M., Heck, S., Truche, L., Bouby, M., Brendlé, J., Hoess, P., and Schäfer, T. (2015). Radionuclide desorption kinetics on synthetic Zn/Ni-labeled montmorillonite nanoparticles. *Geochem. Cosmochim. Acta* **148**, 426–441.
- Zhang, C., Liu, L., Dai, Y., Zhu, K., Liu, Z., and Jia, H. (2022). Molecular dynamics simulations of exchange behavior of radionuclides into montmorillonite: Unraveling the dynamic processes and microscopic structures. *Appl. Clay Sci.* **226**, 106579.
- Perassi, I., and Borgnino, L. (2014). Adsorption and surface precipitation of phosphate onto CaCO₃-montmorillonite: effect of pH, ionic strength and competition with humic acid. *Geoderma* **232**, 600–608.
- Zou, Y., Zhang, R., Wang, L., Xue, K., and Chen, J. (2020). Strong adsorption of phosphate from aqueous solution by zirconium-loaded Ca-montmorillonite. *Appl. Clay Sci.* **192**, 105638.
- Das, T.K., Scott, Q., and Bezbaruah, A.N. (2021). Montmorillonite-iron crosslinked alginate beads for aqueous phosphate removal. *Chemosphere* **281**, 130837.
- Bia, G., De Pauli, C.P., and Borgnino, L. (2012). The role of Fe(III) modified montmorillonite on fluoride mobility: adsorption experiments and competition with phosphate. *J. Environ. Manag.* **100**, 1–9.
- Gatti, M.N., Fernandez, L.G., Sanchez, M.P., and Parolo, M.E. (2016). Aminopropyltrimethoxysilane-silver-modified montmorillonite for the removal of nitrate ions. *Environ. Technol.* **37**, 2658–2668.
- Guiza, S., Brouers, F., and Bagane, M. (2021). Fluoride removal from aqueous solution by montmorillonite clay: Kinetics and equilibrium modeling using new generalized fractal equation. *Environ. Technol. Innovat.* **21**, 101187.
- Jiang, H., and Dai, Y. (2023). Vitamin C modified crayfish shells biochar efficiently remove tetracycline from water: a good medicine for water restoration. *Chemosphere* **311**, 136884.
- Chen, Y., Song, X., and Jiang, Y. (2014). Adsorption kinetics and thermodynamics of BTEX by limestone collected from a karst understand river system. *Earth Sci. Front.* **21**, 180–185.
- Yang, S., He, H., Wu, D., Chen, D., Tan, Z., Yuan, P., and Zhu, J. (2008). Removal of methylene blue by Ti-doped magnetite (Fe₃xTi_xO₄). *Earth Sci. Front.* **15**, 151–154.
- Wu, H., Lin, Y., Wu, J., Zeng, L., Zeng, D., and Du, J. (2008). A preliminary study of surface adsorption of iron oxide minerals for phenol and DOM. *Earth Sci. Front.* **15**, 133–141.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40**, 1361–1403.
- Song, J., Lin, J., and Ren, Y. (2010). Competitive adsorption of binary mixture of leptospirillum ferriphilum and acidithiobacillus caldus onto pyrite. *Biotechnol. Bioproc. Eng.* **15**, 923–930.
- Tan, S.N., and Chen, M. (2012). Early stage adsorption behavior of acidithiobacillus ferrooxidans on minerals I: an experimental approach. *Hydrometallurgy* **119**, 87–94.
- Zou, X., Wu, X., Mo, C., Li, Y., Gao, P., Huang, X., and Liu, L. (2011). Adsorption Equilibrium and Kinetics of Adsorbing Tetracycline Antibiotics on Montmorillonite. *J. Chem. Eng. Chin. Univ.* **25**, 524–528.
- Gong, Z., Wang, J., Wu, L., Wang, X., Lu, G., and Liao, L. (2013). Fabrication of Super Hydrophobic Surfaces on Copper by Solution-immersion. *Chin. J. Chem. Eng.* **21**, 920–926.
- Tang, R., Zhang, H., Lu, C., Liu, K., Wang, Z., Yu, S., Tong, Z., and Junrong. (2021). Adsorption of ciprofloxacin and tetracycline by organically modified magnetic bentonite. *Chem. Ind. Chem. Eng. Prog.* **40**, 6235–6245.
- Maged, A., Iqbal, J., Kharbush, S., Ismael, S., and Bhatnagar, A. (2020). Tuning tetracycline removal from aqueous solution onto activated 2: 1 layered clay mineral: Characterization, sorption and mechanistic studies. *J. Hazard Mater.* **384**, 121320.
- Zhang, J. (2018). Preparation of Magnetic Montmorillonite and its Adsorption

- Properties for Tetracycline and Ciprofloxacin (Nanjing University of Science and Technology).
43. Zhang, H., Shi, M., Xia, M., Wang, F., and Zhao, F. (2021). The Adsorption Mechanism of Montmorillonite for Different Tetracycline Species at Different pH Conditions: the Novel Visual Analysis of Intermolecular Interactions. *Water Air Soil Pollut.* 232, 65.
 44. Wu, M., Yang, H., Wu, Q., Yang, Y., and He, Z. (2023). Adsorption and competition mechanism of tetracycline and erythromycin on montmorillonite: experimental and theoretical investigation. *J. Mol. Liq.* 370, 121037.
 45. Carrado, K. (2000). Synthetic organo-and polymer-clays: preparation, characterization, and materials applications. *Appl. Clay Sci.* 17, 1–23.
 46. Yang, D., Yuan, P., Zhu, J., and He, H. (2007). Synthesis and characterization of antibacterial compounds using montmorillonite and chlorhexidine acetate. *J. Therm. Anal. Calorim.* 89, 847–852.
 47. Ibarburen, C., Naranjo, P., Stötzl, C., Audisio, M., Sham, E., Farfán, T., and Müller, F. (2014). Adsorption of nisin on raw montmorillonite. *Appl. Clay Sci.* 90, 88–95.
 48. Kulshrestha, P., Giese, R.J., and Aga, D. (2004). Investigating the molecular interactions of oxytetracycline in clay and organicmatter: insights on factors affecting its mobility in soil. *Environ. Sci. Technol.* 38, 4097–4105.
 49. Figueroa, R., and Mackay, A. (2005). Sorption of oxytetracycline to iron oxides and iron oxide-rich soils. *Environ. Sci. Technol.* 39, 6664–6671.
 50. Pils, J., and Laird, D. (2007). Sorption of tetracycline and chlortetracycline on K-and Ca-saturated soil clays, humic substances, and clay humic complexes. *Environ. Sci. Technol.* 41, 1928–1933.

STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
TC	MACKLIN	60-54-8
calcium-montmorillonite	MACKLIN	1318-93-0
HCl	LUOYANG CHEMICAL REAGENT FACTORY	7647-01-0
Na(OH)	LUOYANG CHEMICAL REAGENT FACTORY	1310-73-2
CaCl ₂	MACKLIN	10043-52-4
NaCl	MACKLIN	14762-51-7
butyl acetate	Xi'an Sanpu Chemical Reagent Co., Ltd	123-86-4
absolute ethyl alcohol	Sinopharm Chemical Reagent Co., Ltd	64-17-5

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be completed by the primary contact, Dr. Yan Shi (syshiyang@126.com).

Materials availability

In this study, nano-montmorillonite was prepared.

Data and code availability

- All data reported in this paper will be shared by the [lead contact](#) upon request.
- This paper does not report original code.
- Any additional information necessary to reanalyze the data reported in this article is available upon request from the primary contact, Dr. Yan Shi (syshiyang@126.com).

EXPERIMENTAL MODEL AND STUDY PARTICIPANT DETAILS

The models used in the experiment mainly include Quasi-first-order kinetic model, Quasi-second-order kinetic model, Elovich dynamic model and Langmuir isothermal model and Freundlich isothermal model. All the experiments involve no laboratory animals.

METHOD DETAILS

Materials

Tetracycline; molecular formula: C₂₂H₂₄N₂O₈; calcium-montmorillonite, the place of origin is Ningcheng, Inner Mongolia with a CEC of 97.9 mmol/100 g (CEC determined according to the national standard method), as detailed in [Table 1](#); hydrochloric acid (HCl); distilled water; calcium chloride (CaCl₂); sodium hydroxide (Na(OH)) and sodium chloride (NaCl).

Preparation of nano montmorillonite

Referring to the experimental method of Pi Zhenbang, the preparation method of nano-montmorillonite is as follows: (1) Sequentially add the following components to the container: 8.6 g of butyl acetic acid, 25 mL of distilled water, 22 mL of hydrochloric acid, and 32 mL of anhydrous ethanol. Maintain temperature at 60 °C at atmospheric pressure, stir the reaction for 4 h to obtain a gel. (2) Add 5 g of montmorillonite powder to the gel obtained in the previous step. Maintain the temperature at 60 °C at atmospheric pressure and continue stirring for 4 h. Then, proceed with filtration, separation, washing, and finally drying to obtain the end product.

Scanning electron microscopy (SEM) results and analysis

The particle size of sodium calcium-montmorillonite is about 10 μm. It can be seen from [Figure 4A](#) that the particles are gathered by some small layers. The contact angle of calcium-montmorillonite before and after adsorption of tetracycline changed significantly.

Characterization and analysis of contact angle

As shown in [Figure 4B](#), the contact angle of calcium-montmorillonite without adsorption of tetracycline was 33°, while the contact angle became 46.5° after adsorption of tetracycline. It can be inferred that calcium-montmorillonite changed from hydrophilicity before adsorption of tetracycline to hydrophobicity after adsorption of tetracycline.³⁹

X-Ray diffraction (XRD) results and analysis

Comparing with the XRD patterns of calcium-montmorillonite at different initial concentrations in [Figure 4C](#), it can be seen that the peak shifted to a small angle with the increase of solution concentration, indicating that the interlayer spacing of calcium-montmorillonite had changed. There was a strong absorption band near the middle frequency range of 1 030 cm⁻¹ in the infrared spectrum of calcium-montmorillonite, which was caused by the antisymmetric stretching vibration of Si-O-Si of calcium-montmorillonite. It can be seen from [Figure 4D](#) that the interlayer spacing of calcium-montmorillonite increased with the addition of tetracycline, but the interlayer spacing of calcium-montmorillonite after the addition of cations was smaller than that without cationic electrolyte, especially when Ca²⁺ electrolyte was added, showing that the cationic electrolyte formed a competitive relationship with tetracycline and inserted into the layers of calcium-montmorillonite.

Fourier infrared spectroscopy (FT-IR) results and analysis

As shown in [Figure 4E](#), combined with the infrared spectrum, tetracycline molecule had been adsorbed by calcium-montmorillonite. The results of the determination of the specific surface area and pore structure of nanoscale montmorillonite are as follows: BET specific surface area: 247 m²/g; Total pore volume: 9.84 cm³/g; Average particle size: 364 nm. This indicates that nanoscale montmorillonite particles have a relatively substantial specific surface area and a significant pore structure, making them suitable for use as an efficient adsorbent for adsorbing tetracycline.

QUANTIFICATION AND STATISTICAL ANALYSIS

All statistical analyses and software used in this section are primarily Origin2018, and all data in [Figures 3, 5, and 6](#) are averages of three sets of experimental data. We do not use any method in this section to determine whether the data conforms to the assumptions of statistical methods.