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## Comparison of adsorption mechanisms of tungstate ions on different clay minerals

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Tungsten, widely used in industry, can cause ecological risks like soil degradation and plant growth inhibition due to its migration and accumulation in the environment. Studying its adsorption mechanisms helps understand its transformation laws, accurately evaluate ecological risks, and develop control strategies. This study combines first-principles simulations based on DFT (density functional theory) with experiments to explore the different adsorption behaviors of tungsten ( $\text{WO}_4^{2-}$ ) on three clay minerals: kaolinite, montmorillonite, and illite. Adsorption experiments show that lowering the solution pH, increasing the initial concentration, and extending the adsorption time all enhance  $\text{WO}_4^{2-}$  adsorption on the three minerals. A higher pH increases the negative charge on the minerals' surfaces, boosting electrostatic repulsion and reducing  $\text{WO}_4^{2-}$  adsorption. Adsorption kinetics and isotherm studies indicate that the adsorption process on the three minerals follows pseudo-second-order kinetics and the Langmuir model, suggesting chemisorption dominance. The adsorption rate for  $\text{WO}_4^{2-}$  is illite > kaolinite > montmorillonite, while the adsorption capacity at equilibrium is montmorillonite > kaolinite > illite. First-principles studies reveal that  $\text{WO}_4^{2-}$  forms one Al–O coordination bond (1.889 Å) on kaolinite (001), two Si–O bonds (1.799 Å, 1.889 Å) on montmorillonite, and two Si–O bonds (both 1.800 Å) on illite (001). The adsorption of  $\text{WO}_4^{2-}$  on the (001) faces of these minerals is mainly chemisorption, with adsorption energies of  $-166.94 \text{ kJ mol}^{-1}$  (kaolinite),  $-178.52 \text{ kJ mol}^{-1}$  (montmorillonite), and  $-112.65 \text{ kJ mol}^{-1}$  (illite).  $\text{WO}_4^{2-}$  adsorbs most easily on montmorillonite (001) due to its lowest adsorption energy and highest stability, followed by kaolinite (001), and least easily on illite (001).

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## 1 Introduction

Tungsten is a strategic non-renewable metal resource in the national economy and modern defense due to its stable chemical properties, high hardness, and good thermal and electrical conductivity, leading to its widespread use in aerospace, metallurgy, electrochemical devices, the military, manufacturing, and electronics.<sup>1–4</sup> As global tungsten demand grows, so does the mining volume. Waste rock and tailings from tungsten mining and smelting containing tungsten enter the

soil *via* weathering and leaching, causing pollution.<sup>5–8</sup> When soil heavy metals reach certain concentrations, they can migrate into water, air, and crops, ultimately posing direct or indirect risks to human health.<sup>9–12</sup>

Tungsten compounds in soil were long thought to be stable, a perception that has resulted in limited research attention being directed toward this element. Over the past decade, however, studies have demonstrated that tungsten can oxidize into soluble, reactive tungstate ( $\text{WO}_4^{2-}$ ) ions under natural conditions, thereby complicating its environmental behavior.<sup>13,14</sup> Research findings indicate that in acidic soils, tungsten occurs in the form of polytungstates, whereas in alkaline soils, it predominantly exists as  $\text{WO}_4^{2-}$  ions. Tungsten exhibits greater activity and mobility in alkaline soil environments. Similar to other metal anions, the distribution, mobility, and bioavailability of tungsten are pH-dependent.<sup>15–17</sup> Bolan *et al.*<sup>18</sup> emphasized that the solubility and mobility of tungsten are also influenced by its interactions with positively charged iron, aluminum, and manganese oxides, as well as silicate clay minerals. These interactions, in turn, are affected by the variable charge components in soils or sediments. The environmental behavior and potential risks of tungsten in soil have gradually attracted

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the attention of scientific and technological workers, who have begun to explore the adsorption characteristics of tungstate ( $\text{WO}_4^{2-}$ ) on soil mineral components, which is crucial for clarifying the mobility of  $\text{WO}_4^{2-}$  in soil and water systems. Layered silicate minerals are the most common and largest proportion of clay minerals in soil. They have the characteristics of large specific surface area, high chemical and mechanical stability, interlayer structure and high cation exchange capacity, and are important factors affecting the transformation and migration of heavy metal ions in the environment.<sup>19–21</sup> Common layered silicate minerals include kaolinite, illite, montmorillonite, *etc.* Sen Tuna and Braida<sup>22</sup> discovered that as pH increased from 3 to 6, the adsorption of W by kaolinite decreased from 87% to 65%. For other layered silicates, the adsorption of W in montmorillonite and illite also decreases with the increase of pH. Iwai *et al.*<sup>23</sup> investigated the adsorption characteristics of  $\text{WO}_4^{2-}$  on soil clay minerals such as bauxite trihydrate, iron (oxygen) oxides, feldspar and montmorillonite, and analyzed the influence of pH value on the competitive adsorption of  $\text{WO}_4^{2-}$  with  $\text{PO}_4^{3-}$  and  $\text{MoO}_4^{2-}$ . They found that the adsorption affinity of  $\text{WO}_4^{2-}$  was in the order of bauxite trihydrate > feldspar > montmorillonite. Giannantonio Petruzzelli *et al.*<sup>24</sup> studied the adsorption and desorption processes of tungstate ions in three types of soils in the Mediterranean region. They found that the adsorption of tungstate could be described by the Langmuir type equation. The pH value was the main soil property regulating adsorption/desorption, and the soil with a slightly acidic pH value had the largest adsorption capacity. The desorption capacity of alkaline soil is the greatest. The above results indicate that clay minerals, due to their active surface charge, large specific surface area and simple crystal structure, are an important component affecting the transformation and migration of heavy metal ions in the environment. However, the current research mainly focuses on the influence law of the adsorption behavior of tungsten by clay minerals. There are few reports on the influence mechanism of tungsten adsorption by clay minerals and most of them are conventional experimental studies, which cannot be explained from the microscopic perspectives such as molecules and atoms, resulting in the inability to accurately describe the influence mechanism of the interaction between tungsten and the surface of clay minerals.

Density functional theory is a fundamental quantum chemistry research that can obtain microscopic information at the atomic and molecular levels, effectively compensating for the shortcomings of traditional experimental methods. At present, the first-principles method has been successfully applied in research fields such as lattice defect theory,<sup>25</sup> ionic solvation effect,<sup>26,27</sup> and surface and interface adsorption of clay minerals.<sup>28</sup> For instance, He *et al.*<sup>29</sup> conducted a systematic first-principles molecular dynamics (FPMD) simulation to investigate that tungsten exhibited a  $5 \times$  coordination in the  $\text{WO}_4^{2-}$  and  $\text{HWO}_4^-$  systems, while it transformed to a  $6 \times$  coordination in the  $\text{H}_2\text{WO}_4$  system. Chi<sup>30</sup> utilized quantum chemical calculations to point out that the adsorption surface active centers of the substituted structures of montmorillonite, halloysite, and kaolinite have a greater adsorption capacity for cations than the adsorption active centers of the cross-section residual bonds.

Their adsorption capacity for cations is as follows: montmorillonite > halloysite > kaolinite. Quantum chemical calculations can effectively obtain the microstructure and mechanism of  $\text{WO}_4^{2-}$  adsorption on the surface of clay minerals, and also evaluate the adsorption energy of clay minerals to adsorb  $\text{WO}_4^{2-}$ , which can provide guidance for the migration and diffusion of  $\text{WO}_4^{2-}$  in soil.

This paper takes three common clay minerals (kaolinite, montmorillonite, and illite) and  $\text{WO}_4^{2-}$  as the research objects. Through the combination of first-principles and experiments, the differences in the adsorption behavior of kaolinite, montmorillonite, and illite for  $\text{WO}_4^{2-}$  are studied, and the mechanism of the adsorption behavior of  $\text{WO}_4^{2-}$  on the surface of clay minerals is clarified from a microscopic perspective. These findings are conducive to clarifying the migration and transformation laws of tungsten in the soil environment and providing theoretical support for the formulation of tungsten pollution prevention and control strategies.

## 2 Experimental and research methods

### 2.1 Samples and test methods

**2.1.1 Test samples and reagents.** The samples required for the test are shown in Table 1. The clay minerals used in the test, kaolinite, were from Shanghai Aladdin Reagent Co., Ltd, montmorillonite from Shanghai RON Chemical Technology Co., Ltd, and illite from Shanlin Shiyu Mineral Co., Ltd. All of them were of analytical purity. The remaining reagents used in this study were all of analytical grade and provided by Shanghai Aladdin Reagent Co., Ltd.

**2.1.2 Adsorption test method.** The static adsorption method was adopted to study the adsorption performance of different clay minerals for  $\text{WO}_4^{2-}$  under different pH values, different adsorption times, different initial ion concentrations and other conditions. The specific steps of the adsorption test are as follows: take  $0.05 \text{ g} \pm 5 \text{ mg}$  of each of the three clay minerals and place them respectively in 50 mL centrifuge tubes, then divide them into three groups: ① montmorillonite group; ② kaolinite group; ③ illite group, 35 mL of sodium tungstate solution with different initial pH and concentrations was added to each of the three groups of centrifuge tubes for adsorption experiments. The centrifuge tubes filled with samples were placed in a constant temperature shaker, and the rotational speed was adjusted to 200 rpm for oscillation at room temperature. The experiments were designed to sample the three groups of samples at regular intervals with time gradients of 10 min, 30 min, 60 min, 120 min, 240 min, 360 min, 720 min, 1440 min and 2880 min respectively. Before all the supernatants are transferred to the centrifuge tubes, they need to be transferred through a  $0.45 \mu\text{m}$  filter membrane using a disposable syringe. The concentration of  $\text{WO}_4^{2-}$  in the filtrate is tested by Inductively Coupled Plasma Optical Emission Spectrometry (ICP; ULTIMA2, HORIBA Trading (Shanghai) Co., Ltd). The calculation method of the adsorption capacity of  $\text{WO}_4^{2-}$  is shown in formula (1):



Table 1 Experimental samples and reagents

Drug name	Molecular formula	Molecular weight	Manufacturer
Sodium tungstate	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	329.85	Shanghai Aladdin Reagent Co., Ltd
Montmorillonite	Al <sub>2</sub> O <sub>9</sub> Si <sub>3</sub>	282.21	Shanghai RON Chemical Technology Co., Ltd
Illite	K <sub>0.75</sub> Na <sub>0.04</sub> Ca <sub>0.01</sub> Al <sub>2.04</sub> (Si <sub>3.13</sub> Al <sub>0.87</sub> )O <sub>10</sub> (OH <sub>1.86</sub> O <sub>0.14</sub> )	390.79	Shanlin Shiyu Mineral Resources Co., Ltd
Kaolinite	Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> ·2H <sub>2</sub> O	258.16	Shanghai Aladdin Reagent Co., Ltd
Hydrochloric acid	HCl	36.46	Shanghai Aladdin Reagent Co., Ltd
Sodium hydroxide	NaOH	40.00	Shanghai Aladdin Reagent Co., Ltd

$$q = V(C_0 - C_K)/m \quad (1)$$

Among these,  $q$  denotes the adsorption capacity, with the unit: mg g<sup>-1</sup>;  $V$  represents the volume of the solution in the adsorption reaction, unit: L;  $C_0$  is the initial concentration of WO<sub>4</sub><sup>2-</sup> in the solution prior to the reaction, unit: mg L<sup>-1</sup>;  $C_K$  stands for the concentration of WO<sub>4</sub><sup>2-</sup> when the reaction reaches equilibrium, unit: mg L<sup>-1</sup>; and  $m$  refers to the amount of clay mineral used, unit: g. All results are expressed as the mean value.

## 2.2 DFT calculation

**2.2.1 Simulation methods and models.** The DFT calculation is based on the plane wave pseudopotential density functional theory. The relevant calculations are carried out using the Castep module in the Material Studio software. The main dissociation surface (001) surface of three different clay mineral particles (kaolinite, montmorillonite and illite) is studied, and three minerals, namely kaolinite, montmorillonite and illite, are established respectively. According to the molecular formulas of the clay mineral samples in Table 1, it can be known that illite is potassium illite, and kaolinite and montmorillonite are pure kaolinite and pure montmorillonite respectively. Moreover, clay minerals have a certain buffering effect. When the pH solution is ≤4, they will adsorb H atoms, causing the pH solution to tend to 4 and remain stable, which affects the adsorption effect of clay minerals on WO<sub>4</sub><sup>2-</sup>. To compare with the hydroxyl surface of kaolinite (001), the hydroxyl surface of montmorillonite (001) and the hydroxyl surface of potassium illite (001) were selected for the convenience of comparison among the three. The surface structure of the minerals is shown in Fig. 1.

Under the generalized gradient approximation (GGA), the GGA-PBE exchange–correlation functional is used for calculation. The pseudopotentials are selected as OTFG (On The Fly Generated) Ultrasoft. The Brillouin zone integral of the mineral surface adopts the Monkhorst–Pack  $K$ -point grid sampling of (2 × 2 × 1). The truncation of the plane wave can be set to 400 eV. The convergence value of SCF (Self-Consistent Field) is determined to be 2.0 × 10<sup>-6</sup> eV per atom. The BFGS (Broyden–Fletcher–Goldfarb–Shanno) algorithm is adopted for properties such as geometric optimization (inversion space), atomic force and atomic displacement. The convergent tolerance for structural optimization and energy calculation is set as: the energy convergence threshold is 2.0 × 10<sup>-5</sup> eV per atom, the convergence threshold of interatomic force is 0.05 eV Å<sup>-1</sup>, the convergence threshold of atomic displacement is 0.002 Å, and the convergence threshold of internal stress in the crystal is 0.1 GPa.

**2.2.2 Calculation method of adsorption energy.** The differences in the adsorption of WO<sub>4</sub><sup>2-</sup> on different clay mineral (001) surfaces can be evaluated by adsorption energy ( $E_{\text{ads}}$ ), and the calculation method of  $E_{\text{ads}}$  is shown in formula (2):

$$E_{\text{ads}} = E_{\text{Surface/Adsorbate}} - E_{\text{Adsorbate}} - E_{\text{Surface}} \quad (2)$$

In the formula,  $E_{\text{ads}}$  represents the adsorption energy of WO<sub>4</sub><sup>2-</sup> on the (001) plane of the mineral.  $E_{\text{Surface/Adsorbate}}$  is the total energy of the system after WO<sub>4</sub><sup>2-</sup> adsorption on the (001) plane of the mineral.  $E_{\text{Adsorbate}}$  denotes the total energy of WO<sub>4</sub><sup>2-</sup> before adsorption, and  $E_{\text{Surface}}$  stands for the total energy of the mineral's (001) plane before adsorption. The lower the adsorption energy, the more stable the WO<sub>4</sub><sup>2-</sup> adsorption on the mineral (001) plane.

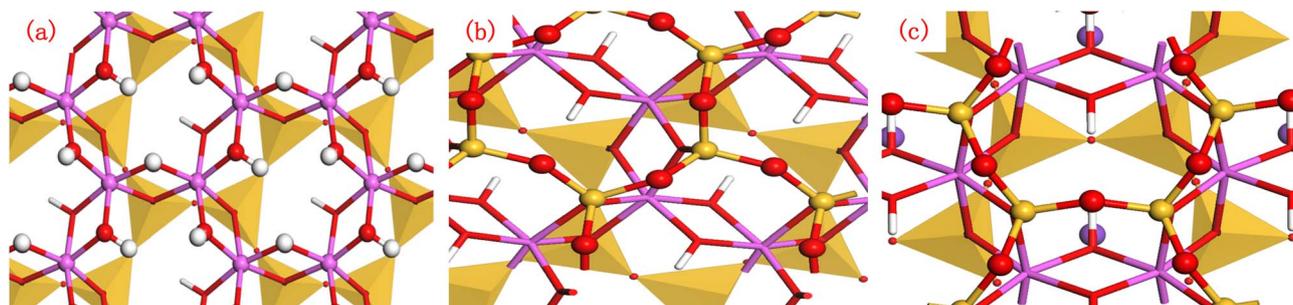


Fig. 1 Structural models of kaolinite (001) surface (a), montmorillonite (001) surface (b), and potassium illite (001) surface (c).



### 3 Results and discussion

#### 3.1 Adsorption test

**3.1.1 The influence of time on adsorption.** The adsorption process is significantly time-dependent, with its kinetic characteristics, equilibrium state, and underlying mechanisms all influenced by time. As the reaction proceeds, the active sites on the adsorbent surface are gradually occupied until saturation is reached, while the remaining adsorption capacity becomes progressively depleted, leading to a minimum in adsorption efficiency. Understanding the impact of time on the adsorption of  $\text{WO}_4^{2-}$  onto different clay minerals facilitates accurate predictions of tungsten migration in soil-plant systems. This provides a scientific basis for soil pollution remediation and environmental risk assessment. To study the effect of contact time on  $\text{WO}_4^{2-}$  adsorption, experiments were conducted with the initial  $\text{WO}_4^{2-}$  concentration fixed at  $100 \text{ mg L}^{-1}$  and  $\text{pH} = 5$ . The adsorption of  $\text{WO}_4^{2-}$  onto various clay minerals was investigated, and the results are shown in Fig. 2.

Fig. 2 directly illustrates the curves of adsorption capacity over time for the three clay minerals. During the initial adsorption stage, all three minerals show a sharp increase in adsorption capacity. Illite has the fastest adsorption rate but the lowest capacity. In the early stage, the rate at which kaolinite adsorbs  $\text{WO}_4^{2-}$  exceeds that of montmorillonite. As time extends, the adsorption capacity of clay minerals for  $\text{WO}_4^{2-}$  peaks and fluctuates within a range, indicating adsorption saturation and stability. At the end of adsorption, montmorillonite shows the highest equilibrium adsorption capacity at  $15.99 \text{ mg g}^{-1}$ , followed by kaolinite at  $12.60 \text{ mg g}^{-1}$  and illite at  $8.21 \text{ mg g}^{-1}$ . Thus, the adsorption capacity order is: montmorillonite > kaolinite > illite.

**3.1.2 The influence of concentration on adsorption.** The  $\text{WO}_4^{2-}$  concentration is a key factor in its adsorption on clay minerals. It affects the occupation of active sites, adsorption driving force, and mechanism. Within the range of low initial concentrations, the adsorption capacity increases significantly

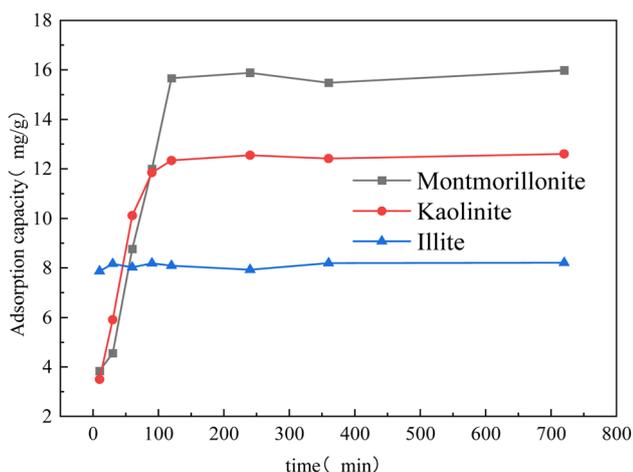


Fig. 2 The influence of time on the adsorption of  $\text{WO}_4^{2-}$  by clay minerals.

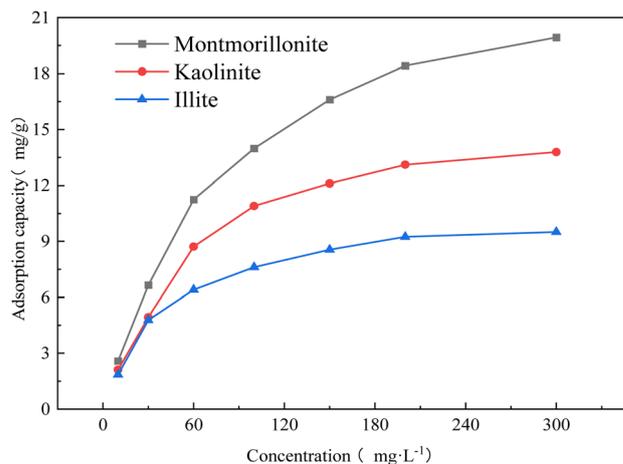


Fig. 3 The influence of initial concentration on the adsorption of  $\text{WO}_4^{2-}$  by clay minerals.

as the initial concentration rises, which is likely due to the fact that the active sites on the adsorbent surface are not yet fully occupied.<sup>31,32</sup> At moderate concentrations, active site occupation slows the adsorption capacity growth. At high concentrations, near-saturation stabilizes adsorption capacity. With a fixed pH of 5 and 12-hour adsorption time, experiments on kaolinite, montmorillonite, and illite adsorption of  $\text{WO}_4^{2-}$  were carried out, and the results are shown in Fig. 3.

Fig. 3 shows the trends in the adsorption capacity of three clay minerals for  $\text{WO}_4^{2-}$  as a function of concentration. Over the range of  $0\text{--}300 \text{ mg L}^{-1}$ , the adsorption capacity of kaolinite, montmorillonite, and illite for  $\text{WO}_4^{2-}$  increases with rising  $\text{WO}_4^{2-}$  concentration; however, this rate of increase gradually slows as active sites on the clay mineral surfaces become occupied. Illite's adsorption capacity approaches its maximum value with only slight further increases, whereas montmorillonite's adsorption capacity is less affected and continues to rise steadily with increasing  $\text{WO}_4^{2-}$  concentration. The maximum adsorption capacities of the three clay minerals across the tested concentration range are as follows: montmorillonite at  $19.93 \text{ mg g}^{-1}$ , kaolinite at  $13.79 \text{ mg g}^{-1}$ , and illite at  $9.50 \text{ mg g}^{-1}$ . Montmorillonite thus exhibits the most superior adsorption performance, with the final adsorption capacities following the order: illite < kaolinite < montmorillonite.

**3.1.3 The influence of pH on adsorption.** The solution pH significantly affects tungsten adsorption in soils by influencing the surface charge of clay minerals, thereby impacting tungsten adsorption efficiency. It is a key factor in the adsorption and desorption of  $\text{WO}_4^{2-}$  by clay minerals. Different clay minerals have varying surface charge types and pH sensitivities. To explore this relationship, experiments were conducted at a fixed initial  $\text{WO}_4^{2-}$  concentration of  $100 \text{ mg L}^{-1}$  and an adsorption time of 24 hours. The results, presented in Fig. 4, show how  $\text{WO}_4^{2-}$  adsorption by different clay minerals varies with pH.

Fig. 4 shows the adsorption of  $\text{WO}_4^{2-}$  by clay minerals at different pH levels. At pH 3, all three minerals—montmorillonite, kaolinite, and illite—exhibit maximum adsorption capacities of  $19.162 \text{ mg g}^{-1}$ ,  $15.932 \text{ mg g}^{-1}$ , and  $8.108 \text{ mg g}^{-1}$ ,



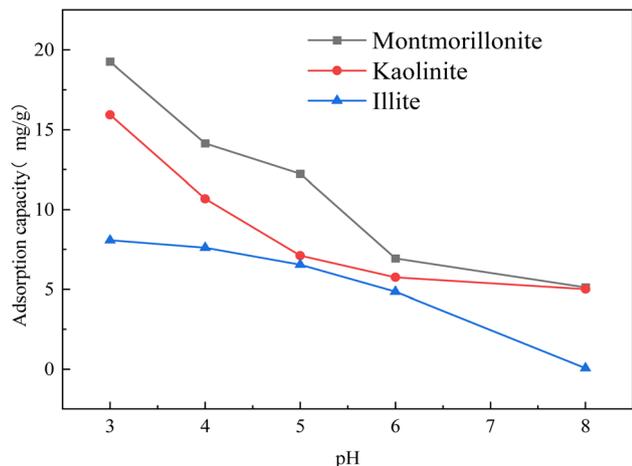


Fig. 4 The influence of pH on the adsorption of  $\text{WO}_4^{2-}$  by clay minerals.

respectively. Thus, the adsorption capacity order is montmorillonite > kaolinite > illite. As pH increases, the adsorption capacity decreases. This is because when the solution pH exceeds 4, the clay minerals' surfaces release H atoms, stabilizing the solution pH at around 4 and increasing the surface negative charge. The resulting electrostatic repulsion between the minerals and  $\text{WO}_4^{2-}$  reduces adsorption. At pH 8, the adsorption capacities drop to  $5.122 \text{ mg g}^{-1}$  for montmorillonite,  $5.011 \text{ mg g}^{-1}$  for kaolinite, and  $0.058 \text{ mg g}^{-1}$  for illite.

### 3.2 Adsorption kinetics

Adsorption kinetic models, crucial for understanding and predicting adsorption processes, describe the adsorption rate and time-dependent changes. They aid in optimizing adsorption design, setting process parameters, and selecting adsorbent materials. The pseudo-first-order and pseudo-second-order kinetic models are widely used. The pseudo-first-order model,

derived from Lagergren's equation, assumes that the adsorption rate is governed by the equilibrium between surface adsorption and desorption. In contrast, the pseudo-second-order model accounts for chemisorption or electron-sharing processes, as well as interactions between the adsorbent and adsorbate throughout the entire process. This study explores the adsorption kinetics of  $\text{WO}_4^{2-}$  onto montmorillonite, kaolinite, and illite. Adsorption data at different time points was collected and fitted to these two models to determine kinetic parameters. The goal is to reveal the adsorption rate characteristics and mechanisms of the three minerals for  $\text{WO}_4^{2-}$ , offering theoretical and technical guidance for using clay minerals in  $\text{WO}_4^{2-}$  pollution control. The model results and fitting parameters are shown in Fig. 5 and Table 2.

As shown in Fig. 5 and Table 2, the pseudo-second-order kinetic model has higher  $R^2$  values than the pseudo-first-order model for the adsorption of  $\text{WO}_4^{2-}$  onto montmorillonite, kaolinite, and illite. This suggests that the pseudo-second-order model better fits the adsorption behavior of these minerals toward  $\text{WO}_4^{2-}$ . The pseudo-second-order model considers the entire adsorption process, where the rate is influenced by the concentration of the adsorbate and may involve multiple adsorption sites and chemical interactions. From the pseudo-second-order model, the adsorption rates of  $\text{WO}_4^{2-}$  for montmorillonite, kaolinite, and illite are  $0.0014$ ,  $0.0042$ , and  $0.0717 \text{ mg g}^{-1} \text{ min}^{-1}$ , respectively. Thus, the adsorption rate order is illite > kaolinite > montmorillonite, with illite reaching equilibrium first. The equilibrium adsorption capacities ( $q_e$ ) are  $17.19 \text{ mg g}^{-1}$  for montmorillonite,  $13.03 \text{ mg g}^{-1}$  for kaolinite, and  $8.21 \text{ mg g}^{-1}$  for illite. Therefore, the final adsorption capacity order is montmorillonite > kaolinite > illite, indicating montmorillonite has the best adsorption performance for  $\text{WO}_4^{2-}$ .

### 3.3 Adsorption isotherm

Adsorption isotherms are curves that describe the relationship between adsorbate concentration and adsorption capacity at

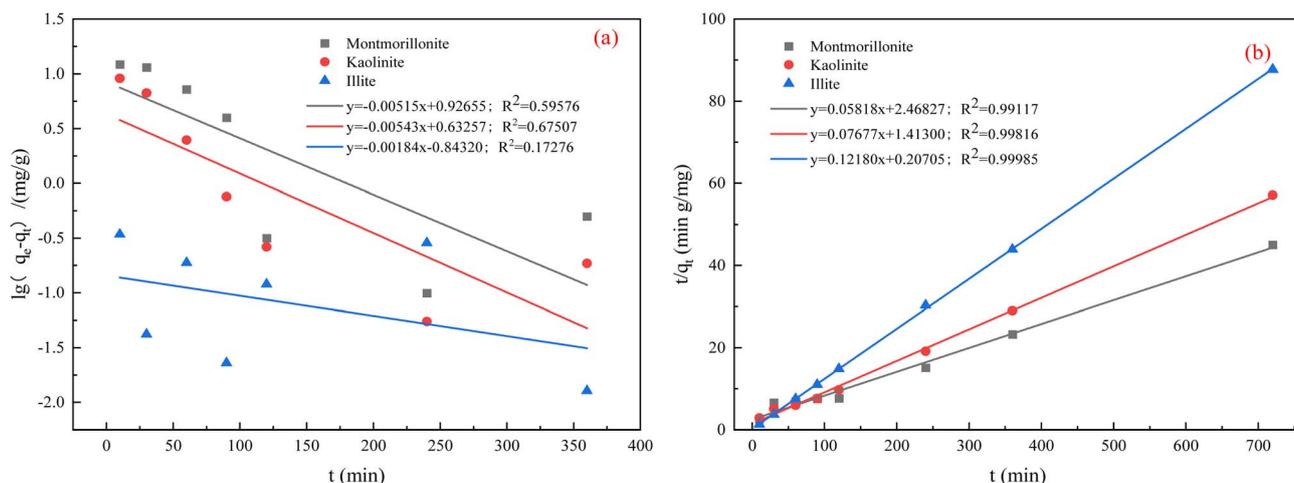


Fig. 5 (a) Quasi-first-order kinetic models of adsorption of  $\text{WO}_4^{2-}$  by three clay minerals; (b) quasi-second-order kinetic models of adsorption of  $\text{WO}_4^{2-}$  by three clay minerals.



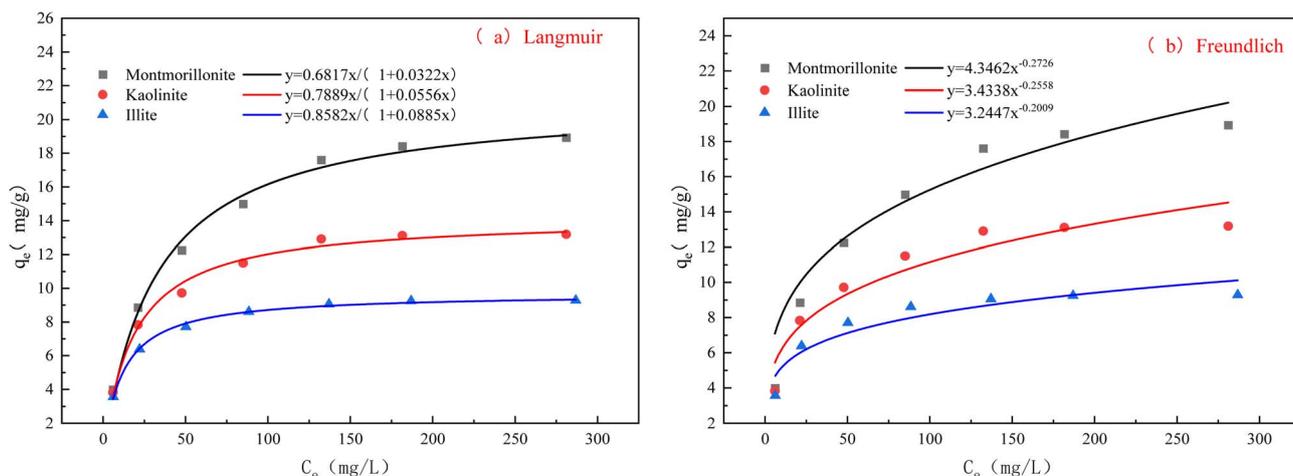
Table 2 Kinetic fitting parameters of  $\text{WO}_4^{2-}$  adsorption by three clay minerals<sup>a</sup>

Sample	W(vi)		Quasi-first-order dynamic model		Quasi-second-order dynamic model		
	$C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R^2$
Montmorillonite	100	8.44	0.0119	0.59576	17.19	0.0014	0.99117
Kaolinite	100	4.29	0.0125	0.67507	13.03	0.0042	0.99816
Illite	100	6.97	0.0042	0.17276	8.21	0.0717	0.99985

<sup>a</sup> In the table,  $C_0$  is the initial adsorption concentration,  $q_e$  is the adsorption capacity at equilibrium,  $K_1$  is the quasi-first-order kinetic rate constant,  $K_2$  is the quasi-second-order kinetic rate constant, and  $R^2$  is the coefficient of determination.

equilibrium under constant temperature. They aid in evaluating an adsorbent's capacity for a specific adsorbate and provide data for thermodynamic and kinetic analyses. The Langmuir model, which assumes monolayer adsorption on a uniform surface with no intermolecular interactions, is well-suited for such processes. In contrast, the Freundlich model is empirical and applies to multilayer adsorption or adsorption on heterogeneous surfaces.<sup>33</sup> In this study, adsorption data of  $\text{WO}_4^{2-}$  solutions with varying initial concentrations onto three clay minerals were used to construct Langmuir and Freundlich isotherm curves (Fig. 6). By fitting and analyzing these models, we can gain a comprehensive understanding of  $\text{WO}_4^{2-}$  adsorption characteristics on the three minerals, uncover the adsorption mechanisms, and compare the adsorption performance of different minerals toward  $\text{WO}_4^{2-}$ .

Fig. 6 shows the Langmuir and Freundlich adsorption isotherm models of the adsorption behavior of  $\text{WO}_4^{2-}$  by three clay minerals. The relevant isothermal parameters are presented in Table 3. When evaluating the applicability of these two models, the correlation coefficient  $R^2$  is a key indicator, which can provide a more intuitive understanding of which model can describe the adsorption process more accurately. By fitting the isothermal models of  $\text{WO}_4^{2-}$  adsorption of three clay minerals, it was found that both the Langmuir model and the Freundlich model could explain the adsorption behavior of  $\text{WO}_4^{2-}$ , but the correlation coefficient  $R_L^2$  of the Langmuir model was greater than that  $R_F^2$  of the Freundlich model. It indicates that the Langmuir model can be better used to explain the adsorption behavior of  $\text{WO}_4^{2-}$  on the surface of clay minerals. According to the Langmuir equation calculation, the

Fig. 6 (a) Langmuir models of adsorption of  $\text{WO}_4^{2-}$  by three clay minerals; (b) Freundlich model of adsorption of  $\text{WO}_4^{2-}$  by three clay minerals.Table 3 Fitting parameters of the Langmuir model and the Freundlich model<sup>a</sup>

Sample	Langmuir model			Freundlich model		
	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R_L^2$	$K_F$ ( $\text{L g}^{-1}$ )	$n$	$R_F^2$
Montmorillonite	21.18	0.0322	0.9914	4.3462	0.2726	0.9328
Kaolinite	14.18	0.0556	0.9882	3.4338	0.2558	0.8968
Illite	9.70	0.0885	0.9962	3.2447	0.2009	0.8684

<sup>a</sup> In the table,  $q_{\text{max}}$  is the maximum adsorption capacity,  $K_L$  is the Langmuir equilibrium constant,  $K_F$  is the Freundlich constant,  $n$  is the Freundlich exponent, and  $R^2$  is the coefficient of determination.



equilibrium adsorption capacities of  $\text{WO}_4^{2-}$  by montmorillonite, kaolinite and illite are  $21.18 \text{ mg g}^{-1}$ ,  $14.18 \text{ mg g}^{-1}$  and  $9.70 \text{ mg g}^{-1}$  respectively. The adsorption equilibrium constants  $K_L$  are  $0.03 \text{ L mg}^{-1}$ ,  $0.06 \text{ L mg}^{-1}$ , and  $0.09 \text{ L mg}^{-1}$ . It indicates that the adsorption capacity of the three clay minerals for  $\text{WO}_4^{2-}$  at adsorption equilibrium is: montmorillonite > kaolinite > illite. In addition, the  $n$  value (adsorption capacity index) in the Freundlich adsorption model is used as an indicator to measure the strength of adsorbing heavy metals. The larger the  $n$  value, the better the adsorption performance. The  $n$  values of adsorbing  $\text{WO}_4^{2-}$  by montmorillonite, kaolinite and illite are relatively small, which are 0.27, 0.26 and 0.20 respectively. It indicates that the adsorption of  $\text{WO}_4^{2-}$  by montmorillonite, kaolinite and illite is relatively difficult.

### 3.4 First-principles study on the adsorption of $\text{WO}_4^{2-}$ on different clay mineral (001) surfaces

**3.4.1 Analysis of adsorption energy and structural parameters of  $\text{WO}_4^{2-}$  on different clay mineral (001) surfaces.** To discuss the adsorption differences of  $\text{WO}_4^{2-}$  in three different clay minerals, namely kaolinite, montmorillonite and illite, Fig. 7 shows the adsorption equilibrium configurations of  $\text{WO}_4^{2-}$  on the (001) surface of kaolinite, montmorillonite and potassium illite (001) surface respectively. The numbers in the figure represent the bond length values, with the unit of Å. Table 4 shows the adsorption energy and structural parameters

of  $\text{WO}_4^{2-}$  on the kaolinite (001) surface, montmorillonite (001) surface and potassium illite (001) surface. It can be known from Fig. 7 and Table 4 that one O atom in  $\text{WO}_4^{2-}$  is adsorbed on the kaolinite (001) surface by forming an Al–O coordination bond with one Al atom on the kaolinite (001) surface, and the bond length of the Al–O coordination bond is  $1.889 \text{ Å}$ . On the (001) face of montmorillonite and the (001) face of potassium illite, the two O atoms in  $\text{WO}_4^{2-}$  are adsorbed on the mineral surface by forming  $\text{Si}_1\text{–O}_1$  and  $\text{Si}_2\text{–O}_2$  coordination bonds with the two Si atoms on the (001) face of montmorillonite and the (001) face of potassium illite. The bond lengths of the  $\text{Si}_1\text{–O}_1$  and  $\text{Si}_2\text{–O}_2$  coordination bonds formed by the adsorption of  $\text{WO}_4^{2-}$  on the (001) face of montmorillonite are  $1.799 \text{ Å}$  and  $1.835 \text{ Å}$ , respectively, and those formed by the adsorption of  $\text{WO}_4^{2-}$  on the (001) face of potassium illite are  $1.800 \text{ Å}$  and  $1.800 \text{ Å}$ .

The adsorption of  $\text{WO}_4^{2-}$  on the (001) surfaces of kaolinite, montmorillonite, and potassium illite is chemical. With an adsorption energy of  $-178.52 \text{ kJ mol}^{-1}$ ,  $\text{WO}_4^{2-}$  is most stable on montmorillonite (001). Next is kaolinite (001) at  $-166.94 \text{ kJ mol}^{-1}$ , and then potassium illite (001) at  $-112.65 \text{ kJ mol}^{-1}$ , indicating the weakest adsorption there. Overall,  $\text{WO}_4^{2-}$  adsorption strength on the three clay minerals ranks as: montmorillonite (001) > kaolinite (001) > potassium illite (001).

**3.4.2 Electronic density of states analysis of the adsorption effect of  $\text{WO}_4^{2-}$  on the (001) surface of different clay minerals.** Fig. 8 presents the density of states (DOS) distribution curves for

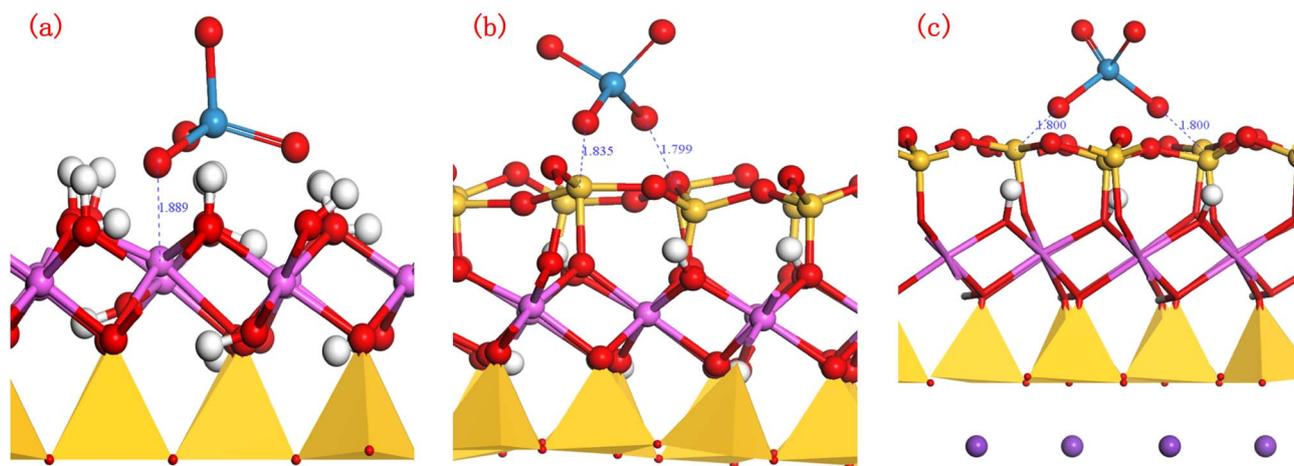


Fig. 7 Adsorption equilibrium configuration diagrams of  $\text{WO}_4^{2-}$  on kaolinite (001) surface (a), montmorillonite (001) surface (b), and potassium illite (001) surface (c).

Table 4 Adsorption energy and structural parameters of  $\text{WO}_4^{2-}$  on the kaolinite (001) surface, montmorillonite (001) surface, and potassium illite (001) surface

Adsorption configuration	$N_{\text{M-O}}^a$	$R_{\text{M-O}}^b/\text{Å}$	$R_{\text{La-O}}^c/\text{Å}$	$E_{\text{ads}}^d/\text{kJ mol}^{-1}$
$\text{WO}_4^{2-}$ —kaolinite (001) surface	1	1.889	1.889	-166.94
$\text{WO}_4^{2-}$ —montmorillonite (001) surface	2	1.835, 1.799	1.817	-178.52
$\text{WO}_4^{2-}$ —illite (001) surface	2	1.800, 1.800	1.800	-112.65

<sup>a</sup> M–O number of bonds. <sup>b</sup> M–O key length. <sup>c</sup> M–O average key length. <sup>d</sup> Adsorption energy.



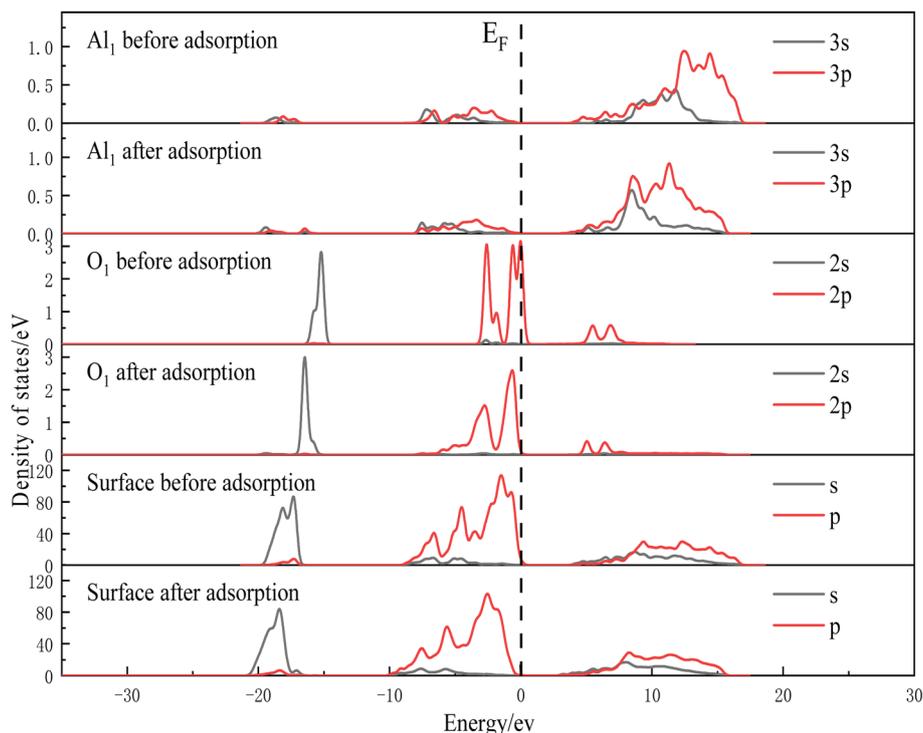


Fig. 8 Al–O atoms and surface state densities of  $\text{WO}_4^{2-}$  before and after adsorption on the kaolinite (001) surface.

$\text{WO}_4^{2-}$  adsorbed on the kaolinite (001) surface, with the Fermi level ( $E_F$ ) set to zero (marked by a vertical dashed line).  $\text{O}_1$  is the  $\text{WO}_4^{2-}$  atom bonding with kaolinite, and  $\text{Al}_1$  is the kaolinite surface atom bonding with  $\text{O}_1$ . The DOS near the Fermi level for  $\text{Al}_1$  mainly comes from its 3p states, while for  $\text{O}_1$ , it mainly comes from its 2p states. After adsorption, the DOS of  $\text{Al}_1$  and  $\text{O}_1$  shift left to lower energies, and the kaolinite surface DOS also moves to lower energies. The 2p states of  $\text{O}_1$  become more non-localized post-adsorption, while the 2s and 2p states of  $\text{Al}_1$  remain non-localized with little change. New, weak peaks appear for  $\text{O}_1$ 's 2s and 2p orbitals at  $-19.5$  eV and  $\text{Al}_1$ 's 3s and 3p orbitals at  $-16.4$  eV, suggesting hybridization between  $\text{Al}_1$  and  $\text{O}_1$ .

Table 5 presents the Mulliken population analysis of  $\text{Al}_1$  and  $\text{O}_1$  in  $\text{WO}_4^{2-}$  before and after adsorption on the kaolinite (001) surface. After adsorption,  $\text{O}_1$  loses electrons from its 2s orbital and gains electrons in its 2p orbital, gaining 0.05 electrons overall (charge changes from  $-0.89$  to  $-0.94$ ).  $\text{Al}_1$  mainly loses

Table 5 Mulliken charge distribution of Al–O atoms before and after adsorption of  $\text{WO}_4^{2-}$  on the kaolinite (001) surface

Species	s	p	d	f	Total	Charge/e
$\text{Al}_1$ before	0.47	0.71	0.00	0.00	1.18	1.82
$\text{Al}_1$ after	0.47	0.68	0.00	0.00	1.15	1.85
Charge	0.00	$-0.03$	0.00	0.00	$-0.03$	0.03
$\text{O}_1$ before	1.90	4.99	0.00	0.00	6.89	$-0.89$
$\text{O}_1$ after	1.87	5.07	0.00	0.00	6.94	$-0.94$
Charge	$-0.03$	0.08	0.00	0.00	0.05	$-0.05$

electrons from its 3p orbital, losing 0.03 electrons overall (charge changes from 1.82 to 1.85).

Fig. 9 shows the density of states distribution curves of  $\text{WO}_4^{2-}$  atoms before and after adsorption on the montmorillonite (001) surface. The energy of  $E_F$  at the Fermi level is set as zero (indicated by the vertical dotted line in the figure). Among them,  $\text{O}_1$  and  $\text{O}_2$  atoms are the atoms in  $\text{WO}_4^{2-}$  that form bonds with the surface of montmorillonite, while  $\text{Si}_1$  and  $\text{Si}_2$  atoms are the atoms on the surface of montmorillonite that form bonds with  $\text{O}_1$  and  $\text{O}_2$ . It can be seen from the figure that the density of states of  $\text{Si}_1$  and  $\text{Si}_2$  atoms near the Fermi level is mainly contributed by the 3p state, while the density of states of  $\text{O}_1$  and  $\text{O}_2$  atoms near the Fermi level is mainly contributed by the 2p state. After adsorption, the densities of states of  $\text{Si}_1$  and  $\text{Si}_2$  atoms and  $\text{O}_1$  and  $\text{O}_2$  atoms move as a whole to the left low-energy direction, indicating that the electron cloud density of Si–O atoms increases relatively. The binding energy of electrons decreases and the interaction of Si–O atoms increases. The localization of the 2p state of  $\text{O}_1$  and  $\text{O}_2$  atoms before adsorption is very strong. After adsorption, the 2p state at the Fermi level changes from a narrow peak to a wide peak, and the double peak becomes multiple peaks, indicating that the non-localization of  $\text{O}_1$  and  $\text{O}_2$  is enhanced. However, the peak density of the 3s state of  $\text{Si}_1$  and  $\text{Si}_2$  atoms decreases, the localization of electrons weakens, and the non-localization is enhanced. New peaks were formed at the 3p orbitals of the  $\text{Si}_1$  atom at  $-17.1$  eV and  $6.4$  eV, the 3p orbitals of the  $\text{Si}_2$  atom at  $-16.9$  eV and  $6.4$  eV, the 2p orbitals of the  $\text{O}_1$  and  $\text{O}_2$  atoms at  $-4.6$  eV and  $4.4$  eV, and the 2s orbitals at  $-19.6$  eV. It indicates that the  $\text{Si}_1$ – $\text{O}_1$  and  $\text{Si}_2$ – $\text{O}_2$  atoms have undergone hybridization reactions.



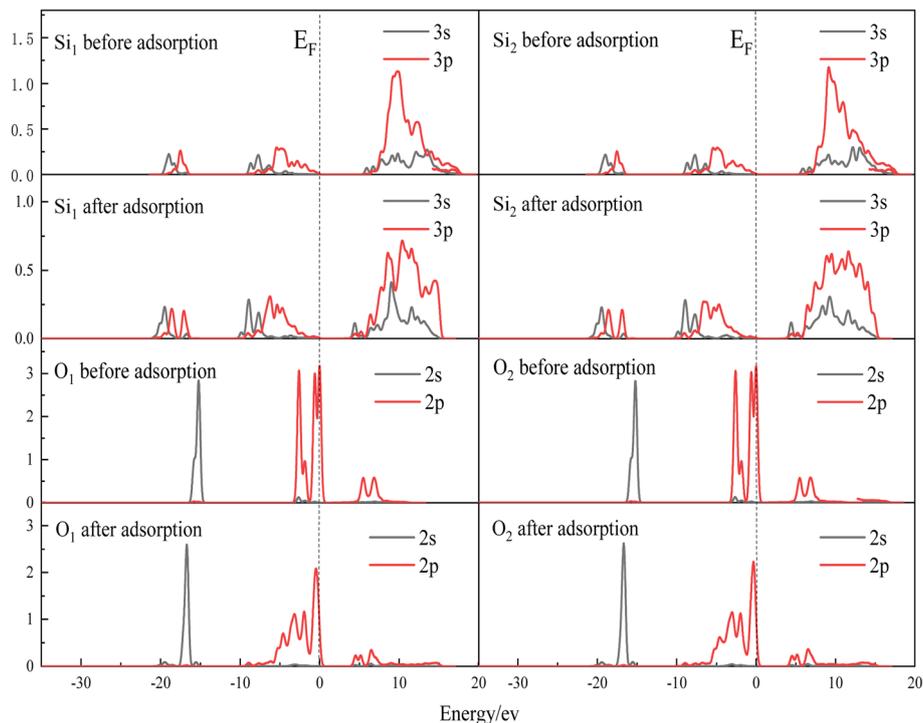


Fig. 9 Si–O atomic state densities of  $\text{WO}_4^{2-}$  before and after adsorption on the (001) surface of montmorillonite.

Table 6 Mulliken charge distribution of Si–O atoms before and after adsorption of  $\text{WO}_4^{2-}$  on the (001) surface of montmorillonite

Species	s	p	d	f	Total	Charge/e
Si <sub>1</sub> before	0.61	1.12	0.00	0.00	1.73	2.27
Si <sub>1</sub> after	0.66	1.21	0.00	0.00	1.87	2.13
Charge	0.05	0.09	0.00	0.00	0.14	−0.14
Si <sub>2</sub> before	0.60	1.12	0.00	0.00	1.72	2.28
Si <sub>2</sub> after	0.67	1.22	0.00	0.00	1.89	2.11
Charge	0.07	0.10	0.00	0.00	0.17	−0.17
O <sub>1</sub> before	1.90	4.98	0.00	0.00	6.88	−0.88
O <sub>1</sub> after	1.86	5.00	0.00	0.00	6.86	−0.86
Charge	−0.04	0.02	0.00	0.00	−0.02	0.02
O <sub>2</sub> before	1.90	4.99	0.00	0.00	6.89	−0.89
O <sub>2</sub> after	1.86	4.99	0.00	0.00	6.85	−0.85
Charge	−0.04	0.00	0.00	0.00	−0.04	0.04

From the analysis of the Mulliken charge distribution of Si–O atoms before and after the adsorption of  $\text{WO}_4^{2-}$  on the montmorillonite (001) surface in Table 6, it can be known that after adsorption, the O<sub>1</sub> and O<sub>2</sub> atoms mainly lose electrons in the 2s orbital and gain electrons in the 2p orbital. The O<sub>1</sub> atom loses 0.04 electrons in the 2s orbital and gains 0.02 electrons in the 2p orbital, losing 0.02 electrons overall. The charge changes from −0.88 to −0.86. The O<sub>2</sub> atom lost 0.04 electrons in the 2s orbital, losing 0.04 electrons as a whole, and its charge changed from −0.89 to −0.85. The Si<sub>1</sub> and Si<sub>2</sub> atoms mainly gain electrons in the 3s and 3p orbitals. The Si<sub>1</sub> atom gains 0.05 electrons in the 3s orbital and 0.09 electrons in the 3p orbital. Overall, it gains 0.14 electrons, and the charge changes from 2.27 to 2.13. The Si<sub>2</sub>

atom gains 0.07 electrons in the 3s orbital, 0.10 electrons in the 3p orbital, and a total of 0.17 electrons, with the charge changing from 2.28 to 2.11.

Fig. 10 shows the density of states distribution curves of  $\text{WO}_4^{2-}$  atoms before and after adsorption on the potassium illite (001) surface. The energy of  $E_F$  at the Fermi level is set as zero (indicated by the vertical dotted line in the figure). Among them, the O<sub>1</sub> and O<sub>2</sub> atoms are the atoms in  $\text{WO}_4^{2-}$  that form bonds with the illite surface, and the Si<sub>1</sub> and Si<sub>2</sub> atoms are the atoms on the illite surface that form bonds with the O<sub>1</sub> and O<sub>2</sub> atoms. It can be seen from the figure that the density of states of Si<sub>1</sub> and Si<sub>2</sub> atoms near the Fermi energy level is mainly contributed by the 3p state, while the density of states of O<sub>1</sub> and O<sub>2</sub> atoms near the Fermi energy level is mainly contributed by the 2p state. After adsorption, the densities of states of O<sub>1</sub> and O<sub>2</sub> atoms shift significantly to the left low-energy direction overall, indicating that the electron binding energy of Si–O atoms decreases and the interaction increases. The localization of the 3p state of Si<sub>1</sub> and Si<sub>2</sub> atoms before adsorption is very strong. After adsorption, the 3p state at the Fermi level changes from a narrow peak to a wide peak, and the double peak becomes a continuous peak. However, the intensity of the 2s and 2p orbital peaks of O<sub>1</sub> and O<sub>2</sub> atoms after adsorption decreases, and the range of state density peaks widens, indicating that the electronic localization of Si and O atoms weakens and the non-localization is enhanced. The Si<sub>1</sub> and Si<sub>2</sub> atoms are at −21.1 eV and −11.8 eV in the 3s orbital, and at −21.0 eV, 0.43 eV and 1.61 eV in the 3p orbital. The O<sub>1</sub> and O<sub>2</sub> atoms are at −23.4 eV, −19.9 eV and 1.64 eV in the 2s orbital. New peaks were formed at −10.2 eV and 0.81 eV in the 2p



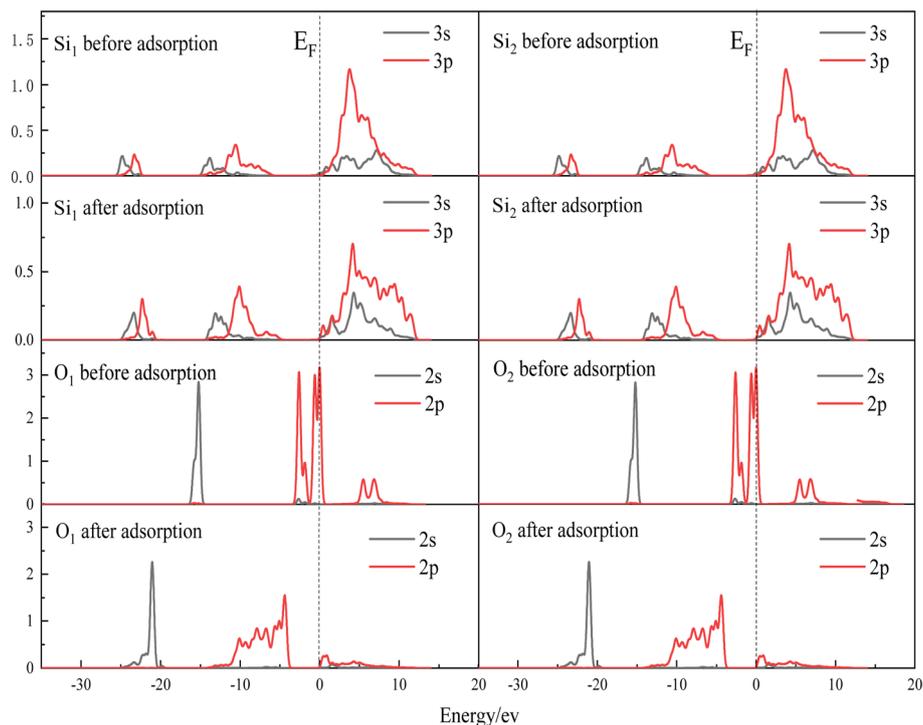


Fig. 10 Si–O atomic state densities before and after adsorption of  $\text{WO}_4^{2-}$  on the potassium illite (001) surface.

Table 7 Mulliken charge distribution of Si–O atoms before and after adsorption of  $\text{WO}_4^{2-}$  on the potassium illite (001) surface

Species	s	p	d	f	Total	Charge/e
Si <sub>1</sub> before	0.62	1.12	0.00	0.00	1.74	2.26
Si <sub>1</sub> after	0.67	1.21	0.00	0.00	1.88	2.12
Charge	0.05	0.09	0.00	0.00	0.14	−0.14
Si <sub>2</sub> before	0.62	1.12	0.00	0.00	1.74	2.26
Si <sub>2</sub> after	0.67	1.21	0.00	0.00	1.88	2.12
Charge	0.05	0.09	0.00	0.00	0.14	−0.14
O <sub>1</sub> before	1.90	4.99	0.00	0.00	6.89	−0.89
O <sub>1</sub> after	1.83	5.05	0.00	0.00	6.88	−0.88
Charge	−0.07	0.06	0.00	0.00	−0.01	0.01
O <sub>2</sub> before	1.90	4.99	0.00	0.00	6.89	−0.89
O <sub>2</sub> after	1.83	5.05	0.00	0.00	6.88	−0.88
Charge	−0.07	0.06	0.00	0.00	−0.01	0.01

orbital, indicating that hybridization reactions occurred in the Si<sub>1</sub>–O<sub>1</sub> and Si<sub>2</sub>–O<sub>2</sub> atoms.

From the analysis of the Mulliken charge distribution of Si–O atoms before and after the adsorption of  $\text{WO}_4^{2-}$  on the potassium illite (001) surface in Table 7, it can be known that after adsorption, O<sub>1</sub> and O<sub>2</sub> atoms mainly lose electrons in the 2s orbital and gain electrons in the 2p orbital. O<sub>1</sub> and O<sub>2</sub> atoms lose 0.07 electrons in the 2s orbital of O<sub>1</sub> and O<sub>2</sub> atoms and gain 0.06 electrons in the 2p orbital. The whole loses 0.01 electrons and the charge changes from −0.89 to −0.88. Both Si<sub>1</sub> and Si<sub>2</sub> atoms gain electrons in the 3s and 3p orbitals. Si<sub>1</sub> and Si<sub>2</sub> atoms gain 0.05 electrons in the 3s orbital and 0.09 electrons in the 3p orbital. As a whole, they gain 0.14 electrons, and the charge changes from 2.26 to 2.12.

## 4 Conclusion

The differences in tungsten adsorption behaviors of different clay minerals (kaolinite, montmorillonite, illite) were studied by combining first-principles simulation based on density functional theory with experiments. The research results show that:

(1) Adsorption tests show that reducing the pH value of the solution, increasing the initial concentration and adsorption time are conducive to the adsorption of  $\text{WO}_4^{2-}$  on the surface of the three clay minerals. With the increase of pH, H atoms are released on the surface of the clay minerals, increasing the negative charge carried on the surface of the clay minerals, and the electrostatic repulsion between the minerals and  $\text{WO}_4^{2-}$  also continuously increases. The adsorption capacity of  $\text{WO}_4^{2-}$  decreases with the increase of pH. The adsorption capacity of the three clay minerals for  $\text{WO}_4^{2-}$  from large to small is: montmorillonite > illite > kaolinite.

(2) The studies of adsorption kinetics and adsorption isotherms show that the adsorption of  $\text{WO}_4^{2-}$  on the surfaces of three clay minerals is more in line with the quasi-second-order kinetics and Langmuir model, and the adsorption is mainly chemical adsorption. The adsorption rates of  $\text{WO}_4^{2-}$  by the three clay minerals from high to low are: illite > kaolinite > montmorillonite. Illite reaches adsorption equilibrium first. At adsorption equilibrium, the adsorption amounts of  $\text{WO}_4^{2-}$  by the three clay minerals are: montmorillonite > kaolinite > illite.

(3) One O atom in  $\text{WO}_4^{2-}$  is adsorbed on the kaolinite (001) surface by forming an Al–O coordination bond with one Al atom on the kaolinite (001) surface. The bond length of the Al–O coordination bond is 1.889 Å. On the (001) face of



montmorillonite and the (001) face of potassium illite, the two O atoms in  $\text{WO}_4^{2-}$  are adsorbed on the mineral surface by forming  $\text{Si}_1\text{-O}_1$  and  $\text{Si}_2\text{-O}_2$  coordination bonds with the two Si atoms on the (001) face of montmorillonite and the (001) face of potassium illite. The bond lengths of the  $\text{Si}_1\text{-O}_1$  and  $\text{Si}_2\text{-O}_2$  coordination bonds formed by the adsorption of  $\text{WO}_4^{2-}$  on the (001) face of montmorillonite are 1.799 Å and 1.889 Å, respectively, and those formed by the adsorption of  $\text{WO}_4^{2-}$  on the (001) face of potassium illite are 1.800 Å and 1.800 Å, respectively.

(4) The first-principles study shows that the adsorption of  $\text{WO}_4^{2-}$  on the kaolinite (001) surface, montmorillonite (001) surface and potassium illite (001) surface is mainly chemical adsorption, and the adsorption energies are  $-166.94 \text{ kJ mol}^{-1}$ ,  $-178.52 \text{ kJ mol}^{-1}$  and  $-112.65 \text{ kJ mol}^{-1}$  respectively. It indicates that the adsorption energy of  $\text{WO}_4^{2-}$  on the (001) surface of montmorillonite is the lowest, the structure is the most stable, and it is the easiest to adsorb on the (001) surface of montmorillonite, followed by the (001) surface of kaolinite.  $\text{WO}_4^{2-}$  is the most difficult to adsorb on the (001) surface of potassium illite.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Due to ethical restrictions, the raw data cannot be made publicly available. However, de-identified data may be obtained from the corresponding author upon reasonable request.

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