Physicochem. Probl. Miner. Process., 60(1), 2024, 183882 | Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp

ISSN 1643-1049

Effect of dry-wet alternation on the adsorption of dissolved organic matter by soil minerals

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Abstract: Dry-wet alternation has an essential effect on soil minerals' adsorption of dissolved organic matter. In this study, kaolin, illite, and hematite were subjected to 0, 1, 3, and 6 dry-wet alternation incubation tests, respectively, and the changes in the characterization of the three minerals were explored by using a BET specific surface area analyzer and an X-ray diffractometer. The effects of different dry-wet alternation treatments on the adsorption of tannic acid and glucose as the representatives of dissolved organic matter were investigated by isothermal and kinetic adsorption tests as well as by different model-fitting methods. The effects of different dry-wet alternation treatments on the adsorption of tannic acid and glucose by the three minerals were investigated by isothermal and kinetic adsorption tests and different model fitting methods. The results showed that alternating dry-wet treatment could change the three minerals' specific surface area and average pore diameter to different degrees. Still, the spacing of the crystal layers did not change significantly. The dry-wet alternation did not alter the adsorption process and tannic acid and glucose adsorption mode. Still, it affected the equilibrium adsorption amount to different degrees, which was illite>hematite>kaolin, and the intensity of the effect was mainly affected by the decrease of the specific surface area of the minerals, which was not related to the change of the average pore diameter and the spacing of the crystal layers.

Keywords: dry-wet alternation, soil minerals, isothermal adsorption, kinetic adsorption

1. Introduction

Soil organic matter is an essential component of the carbon cycle, in which dis-solved organic matter (DOM), such as sugars and organic acids, accounts for a tiny proportion, only 0.04% to 0.22% of the total. Still, it significantly impacts soil organic matter stability, carbon storage, and effective utilization of soil nutrients (Stockmann et al., 2013). Soil clay minerals and iron oxides, which are widely present in the soil, are essential factors affecting soil organic carbon stability, and the intensity of the effect is governed by multiple factors such as their specific surface area, surface charge, interlayer domains, interlayer cation exchange capacity, and intraparticle/interparticle microstructural properties (Schmidt et al., 2011).

Since the 20th century, the frequent occurrence of dry-wet cycles triggered by extreme droughts and precipitation has altered the characteristics of the global hydro-logical cycle, as well as the surface area, layer spacing, porosity, and electrically charged properties of soil clay minerals and iron oxides (Farooq et al., 2022; Stanjek & Marchel, 2008). A mixture of 80% kaolin and 20% bentonite gradually decreases hysteresis as the number of dry-wet cycles increases (Goh et al., 2014). When moisture increases, montmorillonite exhibits more intense swelling in interaction with water. When moisture decreases, it shrinks in volume and produces fissures (Chang et al., 2022). Ilmenite has reversible contraction and expansion under wetting and drying conditions. The degree of contraction/expansion varies by type, and the greater the wet/dry cycle amplitude, the more significant the volume change (Kühnel et al., 2017; Zhou et al., 2022). Repeated soil expansion and contraction triggered by dry-wet cycles in the external environment strongly affect the soil's internal microstructure and pore distribution (Al-Mahbashi et al., 2023). Chen et al. found that the soil strength decreases with the increase in dry-wet

DOI: 10.37190/ppmp/183882

cycles and tends to be constant after 3-4 cycles (Chen et al.，2021). The greater the amplitude of dry-wet cycles, the more surface cracks after damage and the significant decrease in soil strength. Wang Jin et al. showed that sodium montmorillonite increased with the increase in water content, and the layer spacing increased and showed a trend of gradual expansion (Wang & Zeng, 2005). Wang Yingying et al. found that clay mineral deformation gradually stabilized with the increase in the number of cycles (Wang et al., 2014). In rice-wheat cropping systems, dry-wet alternation contributes to the crucial role that iron oxides may play in soil carbon conservation by forming organic-iron complexes (Huang et al., 2020). Frequent dry-wet environments alter the redox environment of the soil, where reactive iron oxides produce strong redox effects, altering the soil iron oxide composition and modulating the pathways of soil organic matter transformation (Huang et al., 2016).

It has been suggested that dry-wet alternation can affect the adsorption strength, quantity, and stability of soil organic matter by changing the characterization of soil clay minerals and iron oxides (Niu et al., 2023; Thomas & Strobel, 2022). However, the relevant studies still need to be improved so far, limiting a more in-depth knowledge of soil organic matter stability. For this reason, kaolinite, illite, and hematite were selected in this study to analyse the effects of different alternating dry-wet treatments on the surface area, average pore size, and crystal layer spacing using indoor incubation tests. Glucose and tannic acid were also selected as representatives of dissolved organic matter to study the effects of alternating dry-wet treatments on the adsorption of soil dissolved organic matter by the three soil minerals. It provides a theoretical basis for a deeper understanding of the effects of soil organic carbon decomposition and transformation as well as the conservation of soil organic matter.

2. Materials and methods

2.1. Materials

Kaolin, Illite, and Hematite were purchased from Shanlin Stone Language Mineral Products Co. The purity was above 98%. Glucose and tannic acid were purchased from Shanghai McLean Reagent Co.

2.2. Materials

2.2.1 Alternating dry-wet incubation test

20 g kaolin was placed in a 250 cm^3 wide-mouth bottle and weighed immediately after adding 8 cm^3 of deionized water. Weigh again after air-drying at a constant temperature of 25 ℃ for 10 days. The difference between the two weights was the weight of the next rehydration. Based on the above method, the dry-wet incubation tests were carried out 0, 1, 3, and 6 times, and the samples were collected to determine the specific surface area, the crystal layer spacing, and the average pore size, with three replicates for each treatment. The culture tests for illite and hematite were the same as for kaolin.

2.2.2 Kinetic adsorption test

Weigh 1 g of the incubated sample, add 100 cm^3 each of deionized water and 400 mg/dm^3 glucose solution (tannic acid concentration of 100 mg/dm^3), aspirate 10 cm^3 of the mixture after 1, 30 min, and 1, 3, 6, 12, and 24 h (1, 5, 10, 20, 30, 60, and 90 min for the tannic acid solution), and centrifuge the sample for 5 min (at a rotational speed of 3000 r/ min), the supernatant was extracted with a 0.45 μm aqueous needle filter, and the glucose concentration was determined using a TOC analyser. The concentration of tannic acid was determined by standard curve method. Configure 0, 10, 20, 30, 40, 50 mg/dm^3 tannic acid standard solution, measure the absorbance at 276 nm with UV spectrophotometer, and get the standard curve of tannic acid. The absorbance of the sample was measured by UV spectrophotometer at 276 nm, and the concentration of tannic acid was obtained by substituting the absorbance into the standard curve. Each treatment was repeated three times.

Fitting the kinetic adsorption process of glucose (tannic acid) of the three minerals using the proposed primary kinetic equation (1) and the proposed secondary kinetic equation (2).

$$In(Q_e - Q_t) = InQ_e - k_1 \times t \tag{1}$$

where Q_e (mg/g) is the adsorbed amount at equilibrium; Q_t (mg/g) is the adsorbed amount at time t; t (min) is the adsorption time; and k_1 (/min) is the velocity constant.

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{kQ_e^2} \tag{2}$$

where k_2 (g/(mg • min)) is the velocity constant.

2.2.2. Isothermal adsorption test

Weigh 0.1 g of the incubated sample, add 10 dm^3 of deionized water and 10 cm^3 of glucose solution with concentration gradients of 0, 50, 100, 150, 300 and 400 mg/dm^3 (tannic acid concentration gradients of 0, 20, 30, 40, 50, 60, 80 and 100 mg/dm^3). After shaking on a thermostatic shaker at 200 r/min for 24 h (4 h for tannic acid solution), the solution was centrifuged for 15 min (at 3000 r/min). Glucose and tannic acid concentrations were determined as in 2.2.2.

Fitting the isothermal adsorption process of glucose (tannic acid) of three minerals using Langmuir equation (3) and Freundlich equation (4).

$$Q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \tag{3}$$

where Q_m (mg/g) is the maximum adsorption amount; K_L (dm^3/mg) is the parameter of adsorption capacity; C_e (mg/ dm^3) is the concentration of glucose (tannic acid) in the solution at adsorption equilibrium.

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where K_F ((mg/g)/(mg/dm^3)) is the adsorption capacity parameter; n is a dimensionless constant.

2.3. Determination of soil mineral characterization

Measurements were made using a 4-station fully automated specific surface area analyser (Micromeritics APSP 2460), and a Bruker X-ray diffractometer (Bruker D8 ADVANCE).

3. Results and discussion

3.1. Characterization of soil minerals

The specific surface area of the three minerals decreased after different dry-wet alternation treatments. Among them, the decrease of kaolinite was relatively small, the change of illite was relatively obvious, showing the characteristic of decreasing with the increase of the number of times, and the decrease of hematite was 0.3 m2/g after the first dry-wet alternation and was stable thereafter; with the increase of the number of dry-wet times, the average pore diameter of kaolinite did not show obvious regular changes, the average pore diameter of illite increased with the increase of the number of dry-wet times, and the average pore diameter of hematite showed the characteristic of increasing 3.4 nm after the first dry-wet alternation and was stable thereafter. The average pore size of hematite showed an increase of 3.4 nm after the first dry-wet alternation and stabilized thereafter. The spacing of the crystal layers of the three minerals did not change significantly after different dry-wet treatments (Table 1).

Table 1. Specific surface area, average pore size, and crystal plane spacing of three minerals after different dry wet alternation treatments

Mineral type	Number of dry-wet cycles	Specific surface area (m^2/g)	Average pore size (nm)	crystal plane spacing (d/Å)
Kaolin	0	14.4	31.1	7.2
	1	14.4	30.6	7.2
	3	14.3	27.9	7.2
	6	14.3	36.7	7.2
Illite	0	28.3	15.4	10.0
	1	27.9	17.8	10.0
	3	27.7	18.9	10.0
	6	27.5	20.1	10.1
Hematite	0	30.7	15.4	2.8
	1	30.4	18.3	2.8
	3	30.5	18.8	2.8

	6	30.4	18.8	2.8

3.2. Effect of dry-wet treatments on adsorption of tannic acid by soil minerals

3.2.1 Characterization of kinetic adsorption of tannic acid adsorption by soil mineral

The number of dry-wet times did not change the time change trend of the adsorption number of tannins by the three minerals, which showed a rapid increase at the initial stage, followed by a slowing down of the increase, and finally reached the adsorption equilibrium. However, the adsorption number of tannins by the same minerals differed among different treatments. There was no significant difference in the adsorption amount of kaolin, and illite showed a decreasing adsorption amount with the increase in the number of dry-wet times; the adsorption amount of hematite showed a significant decrease after the initial treatment, but the increase in the number of times thereafter did not have a strong effect on the adsorption amount (Fig. 1).

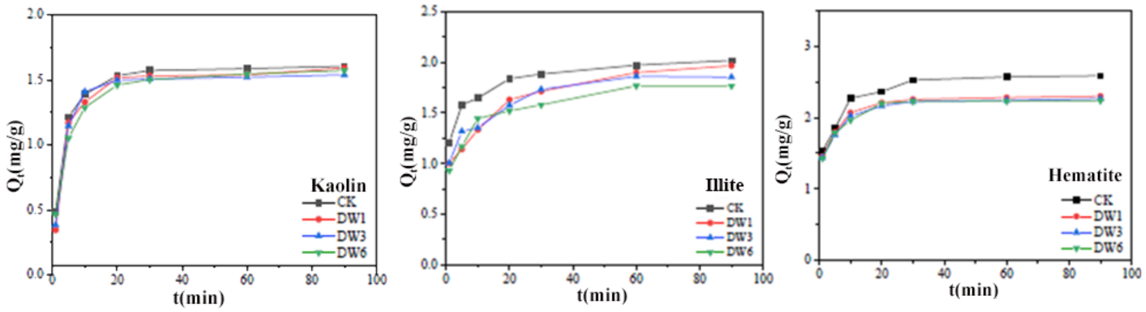

Fig. 1. Time variation curve of tannin adsorption capacity of three minerals after different alternating dry-wet treatments (Note: CK, DW1, DW3, and DW6 are the dry-wet times 0 times, 1 time, 3 times and 6 times, respectively, the same as below)

Table 2. Kinetic adsorption fitting parameters of tannin by three minerals after different alternating dry-wet treatments

Mineral type	Number of dry-wet cycles	Q_e (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			k_1 (1/min)	q_e,1 (mg/g)	R^2	k_2 [g/(mg·min)]	q_e,2 (mg/g)	R^2
kaolin	0	2.021	0.052	0.942	0.956	0.329	1.645	0.999
	1	1.973	0.044	0.940	0.869	0.273	1.614	0.998
	3	1.852	0.052	0.879	0.843	0.335	1.582	0.998
	6	1.671	0.041	0.954	0.936	0.257	1.611	0.999
Illite	0	2.024	0.020	0.799	0.938	0.267	2.045	0.999
	1	1.973	0.020	0.988	0.991	0.124	2.032	0.997
	3	1.855	0.027	0.938	0.967	0.189	1.914	0.998
	6	1.677	0.022	0.866	0.862	0.204	1.817	0.998
Hematite	0	2.593	0.041	1.042	0.949	0.244	2.612	0.999
	1	2.254	0.044	0.907	0.972	0.399	2.325	0.999
	3	2.212	0.041	0.805	0.967	0.390	2.291	0.999
	6	2.242	0.072	1.109	0.993	0.373	2.271	0.999

The results of the above adsorption behaviours were further fitted by the proposed primary kinetic model and the proposed secondary kinetic model (Table 2), which showed that the R^2 of the proposed secondary kinetic model was greater than 0.99. The gap between the theoretical adsorption amount and the experimental saturated adsorption amount was smaller, which could better reflect the adsorption behaviour of tannic acid, indicating that the chemisorption played a dominant role in the adsorption process of tannic acid.

3.2.2 Characterization of isothermal adsorption of tannic acid by soil minerals

The dry-wet treatments did not change the trend of the curve of isothermal adsorption of tannic acid by the three minerals, which was characterized by the rapid increase of adsorption with the increase of concentration. Then, the growth rate slowed down and tended to equilibrium. Under the condition of the same concentration, the difference in adsorption amount of the three minerals between different treatments showed different performances. There was no significant difference in the adsorption amount of kaolin between different treatments. Ilmenite showed the characteristic of decreasing adsorption amount with the increase of the number of dry-wet alternations. Hematite showed a significant decrease in adsorption after the initial dry-wet treatment, but thereafter, there was no significant change in adsorption with the increasing number of times (Fig. 2).

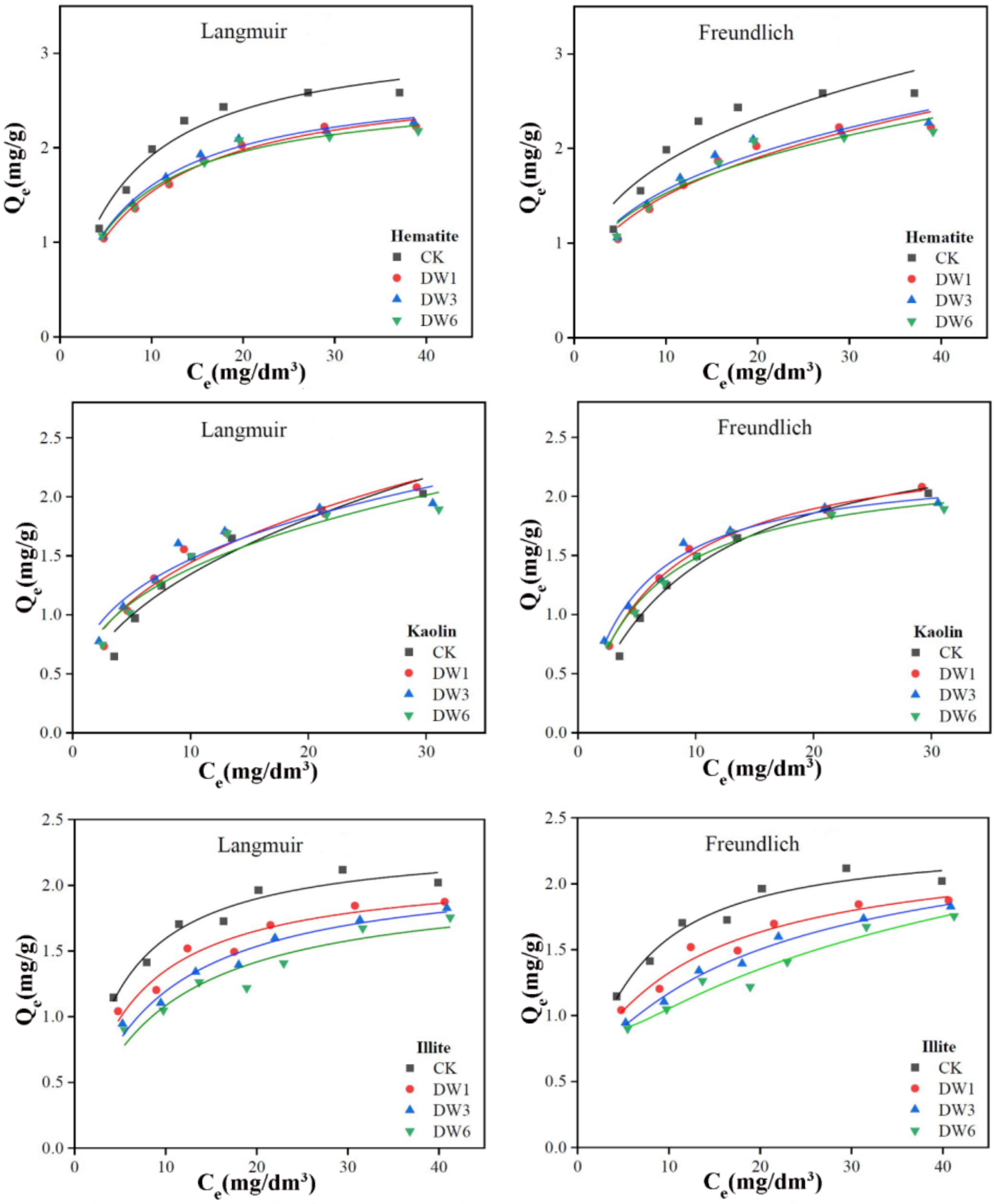

Fig. 2. Isothermal adsorption fitting results of tannin by three minerals after different alternating dry-wet treatments

The results of the above adsorption behaviours fitted with Langmuir model and Freundlich model showed (Table 3) that the Freundlich model fitted with a larger R^2 could better reflect the adsorption behaviour of kaolinite on tannic acid, indicating that the distribution of the adsorption sites of kaolinite was heterogeneous. The adsorption of tannic acid showed non-homogeneous multi-layered adsorption characteristics. In contrast, the Langmuir model can better fit the adsorption behaviour of tannic acid on illite and hematite, and the adsorption behaviour of tannic acid on illite and hematite is monolayer adsorption. Different alternating dry-wet treatments failed to change the adsorption mode of tannic acid on the three minerals.

Table 3. Isothermal adsorption fitting parameters of glucose by three minerals after different alternating dry-wet treatments

Mineral type	Temperature(℃)	Number of dry-wet cycles	Langmuir model				Freundlich model		
			K_L (dm^3/mg)	Q_m (mg/g)	R_L	R^2	K_F[(mg/g)·(mg/ $dm^3)^n$]	n	R^2
Kaolin	25	0	0.108	2.718	0~1	0.884	4.502	1.595	0.999
		1	0.160	2.486	0~1	0.836	4.303	1.508	0.978
		3	0.216	2.289	0~1	0.796	4.302	1.447	0.989
		6	0.181	2.291	0~1	0.821	4.566	1.457	0.989
Illite	25	0	0.490	3.729	0~1	0.938	3.324	1.663	0.875
		1	0.465	3.333	0~1	0.977	2.769	1.875	0.956
		3	0.439	2.711	0~1	0.936	2.405	1.007	0.932
		6	0.427	2.003	0~1	0.944	2.326	1.292	0.933
Hematite	25	0	0.210	3.113	0~1	0.972	0.890	3.129	0.831
		1	0.123	2.781	0~1	0.984	0.685	2.930	0.922
		3	0.139	2.753	0~1	0.984	0.752	3.252	0.902
		6	0.137	2.625	0~1	0.972	0.747	3.121	0.893

3.3. Effect of dry-wet treatments on glucose adsorption by soil minerals

3.3.1 Characterization of kinetic adsorption of glucose by soil minerals

Different dry-wet treatments did not change the three minerals' temporal trends of glucose adsorption. Kaolin adsorption showed an initial rapid increase and reached adsorption equilibrium quickly. The adsorption amount of ilmenite and hematite showed a rapid increase at the initial stage, then the increase slowed down and finally reached the adsorption equilibrium. The adsorption characteristics of the three minerals for glucose were the same as those for tannic acid (Fig. 3).

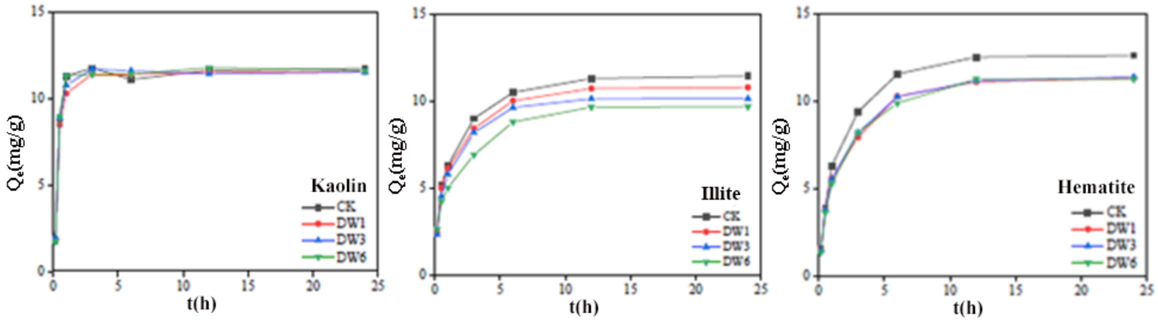

Fig. 3. Time variation curves of glucose adsorption capacity of three minerals after different alternating dry-wet treatments

After fitting the above adsorption behaviours using the proposed primary kinetic model and the proposed secondary kinetic model, the results showed that (Table 4) the R2 after fitting the proposed secondary kinetic model was greater than 0.99. The gap between the theoretical adsorption amount and the experimental saturated adsorption amount was small, which could better reflect the adsorption behaviour of glucose, indicating that the chemisorption played a dominant role in the adsorption process of glucose.

3.2.2. Characterization of isothermal adsorption of glucose by soil minerals

Different dry-wet treatments did not change the trend of isothermal adsorption curves of the three minerals on glucose adsorption amount, and the overall performance of the saturated adsorption amount with the increase of glucose concentration also gradually increased the change characteristics. However, under the same concentration condition, the adsorption amount of glucose by the three minerals between different dry-wet treatments showed certain differences. Among them, there was no significant difference in the adsorption amount between different treatments of kaolin. Ilmenite showed a decrease in adsorption amount with the increase in the number of dry-wet alternations. Hematite showed a significant decrease in adsorption after the initial dry-wet treatment. Still, thereafter, there was no significant change in adsorption with the increase in the number of dry-wet alternations (Fig. 4).

The results after fitting the above adsorption behaviours using Langmuir model and Freundlich model showed that (Table 5), the Freundlich model fitted with a larger R^2 could better reflect the adsorption behaviours of the three minerals on glucose, indicating that the distribution of adsorption sites of the three minerals was heterogeneous. The adsorption of glucose showed a nonlinear trend, exhibiting nonhomogeneous Multilayer adsorption characteristics. Different dry-wet alternating treatments failed to change the adsorption mode of the three minerals on glucose.

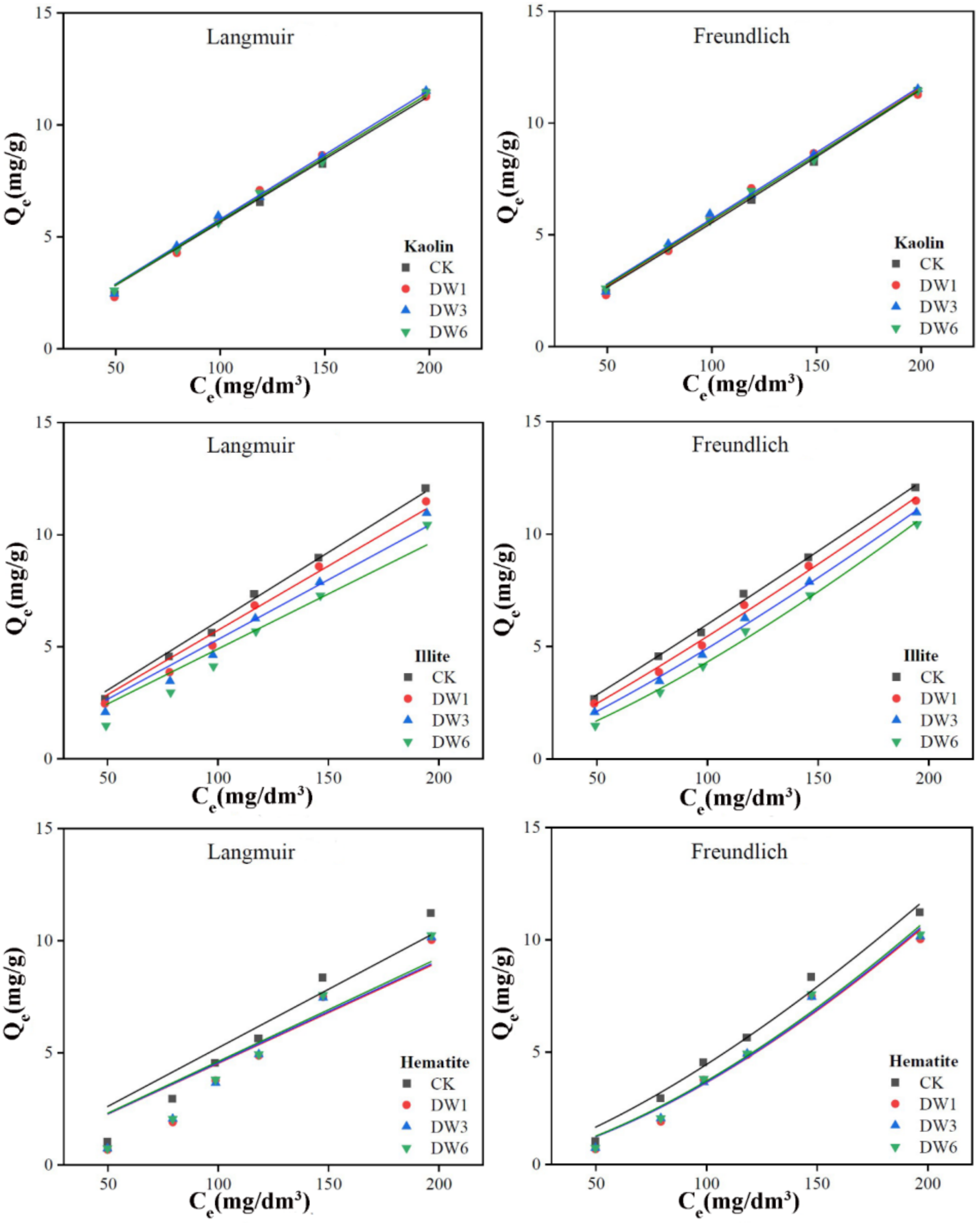

Fig. 4. Isothermal adsorption fitting results of glucose by three minerals after different alternating dry-wet treatments

Table 4. Kinetic adsorption fitting parameters of glucose by three minerals after different alternating dry-wet treatments

Mineral type	Number of dry-wet cycles	Q_e (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			k_1 (1/min)	$q_{e,}1$ (mg/g)	R^2	k^2 [g/(mg·min)]	$q_{e,}2$ (mg/g)	R^2
kaolin	0	11.764	1.522	3.254	0.993	0.593	11.597	0.994
	1	11.583	0.563	2.277	0.949	0.037	11.950	0.998
	3	11.670	1.193	2.871	0.992	0.405	12.142	0.998
	6	11.734	0.448	1.968	0.683	0.426	11.910	0.997
Illite	0	11.432	0.150	2.426	0.993	0.106	11.966	0.999
	1	11.785	0.178	2.449	0.996	0.114	11.349	0.999
	3	10.142	0.194	2.390	0.993	0.124	10.755	0.999
	6	9.678	0.216	2.595	0.964	0.110	10.230	0.993
Hematite	0	12.583	0.176	2.815	0.997	0.055	13.881	0.999
	1	11.295	0.139	2.558	0.997	0.065	12.217	0.999
	3	11.346	0.140	2.571	0.993	0.064	12.290	0.999
	6	11.232	0.142	2.606	0.976	0.057	12.442	0.999

Table 5. Kinetic adsorption fitting parameters of glucose by three minerals after different alternating dry-wet treatments

Mineral type	Tempera-ture (°C)	Number of dry-wet cycles	Langmuir model				Freundlich model		
			K_L (dm^3/mg)	Q_m (mg/g)	R_L	R^2	K_F[(mg/g)·(mg/L)^n]	n	R^2
Kaolin	25	0	6.5×10^{-6}	8.7×10^{3}	0~1	0.993	0.043	0.947	0.996
		1	1.0×10^{-5}	5.5×10^{3}	0~1	0.989	0.046	0.960	0.991
		3	1.2×10^{-5}	4.6×10^{4}	0~1	0.994	0.050	0.973	0.995
		6	9.9×10^{-6}	5.8×10^{4}	0~1	0.997	0.049	0.970	0.998
Illite	25	0	5.9×10^{-7}	1.3×10^{5}	0~1	0.993	0.044	0.937	0.997
		1	2.4×10^{-6}	2.3×10^{4}	0~1	0.978	0.029	0.877	0.993
		3	2.0×10^{-7}	2.6×10^{5}	0~1	0.965	0.018	0.824	0.996
		6	1.2×10^{-6}	4.1×10^{4}	0~1	0.930	0.009	0.746	0.995
Hemati te	25	0	8.3×10^{-7}	6.3×10^{5}	0~1	0.893	6.4×10^{-3}	0.704	0.981
		1	5.7×10^{-7}	7.9×10^{5}	0~1	0.836	2.7×10^{-3}	0.640	0.967
		3	5.8×10^{-7}	7.8×10^{5}	0~1	0.843	2.7×10^{-3}	0.638	0.975
		6	5.9×10^{-7}	7.9×10^{5}	0~1	0.843	2.8×10^{-3}	0.642	0.973

3.3. Adsorption behaviour of three minerals on DOM

The kinetic adsorption process of all three minerals on tannic acid and glucose went through three stages: rapid adsorption, slow adsorption, and equilibrium adsorption. In the early adsorption stage, more active adsorption sites existed on the surface of clay minerals, and DOM molecules were rapidly bound. With the decrease of active sites and smaller adsorption space, coupled with the decrease of DOM content in the system, the adsorption rate slows down. Eventually, it reaches the equilibrium saturation state (Fig. 1 and Fig. 3). Some scholars believe that the adsorption process can be divided into the surface, mesopore, and micropore adsorption in three stages: the first stage is the surface diffusion stage; DOM migrates from the solution to the surface of the mineral particles due to a large number of adsorption sites on the surface of the mineral at the initial stage and the difference between the concentration of DOM in the solution and the mineral particles, the rate of diffusion is speedy; the second stage is the mesopore diffusion stage, the DOM enters into the interior by the surface of the mineral particles, and the diffusion rate becomes slower; the third stage is the microporous diffusion stage, where DOM diffuses inside the mineral particles, and the diffusion rate is greatly reduced until equilibrium due to the concentration difference becomes smaller (Gao et al., 2023). Since the volume of the two DOM adsorbents in this test is too large relative to the mineral pores, it is impossible or difficult for adsorption and diffusion behaviours to occur in the mineral micropores; it is inferred that surface diffusion and mesopore diffusion are the main mechanisms of DOM adsorption by the three minerals.

Although the adsorption characteristics of the three minerals for tannic acid and glucose showed the same behaviour, the equilibrium adsorption amount and arrival time for both showed some differences. The equilibrium adsorption amount of glucose was larger, and the equilibrium arrival time was longer than that of tannic acid. For example, the equilibrium adsorption amounts of kaolin for tannic acid and glucose were around 1.5 mg/g and 11.5 mg/g, respectively. The time to reach the equilibrium was 30 min and 3 h, respectively, and the same characteristics were also shown for il-lite and hematite (Fig. 1 and Fig. 3). This may be attributed to the fact that tannins belong to large organic acids with high molecular mass and thus can reach the mineral surface more rapidly and occupy the active adsorption sites on the surface, but also lead to the formation of a large spatial site resistance, which hinders the further adsorption process thereafter (Shaker et al., 2012; Das & Mahiuddin, 2007). In addition, the presence of a large amount of bound water on the surface of soil minerals, which is endowed on the surface of clay minerals in the form of multilayer physical adsorption, may have limited hindrance to the diffusion of larger molecular weight tannins to the mineral surface (Pedarla et al., 2012). It has been shown that when glucose occupies the adsorption sites of minerals, it forms layers of organic molecules stacked on top of each other on the mineral surface, creating potential adsorption sites for the continued adsorption of glucose (Kleber et al., 2007). As the content of organic matter increases, the organic matter can "enter" the "mineral organic matter" complex on the mineral surface more easily, forming a layered structure on the mineral surface and showing a larger adsorption capacity (Sollins et al., 2006).

The proposed secondary kinetic model better fits the adsorption behaviours of the two DOMs on the three minerals, suggesting that in addition to van der Waals forces, there may be hydrogen bonding and hydrophobic associations between the minerals and the DOMs.

3.4. Effect of dry-wet alternation on DOM adsorption by kaolin

Kaolin is a kind of non-expansive clay mineral with high stability. The unit structure between crystal layers is tightly bonded by van der Waals force or hydrogen bonding (Yu et al., 2018), and the spacing of crystal layers is about 7.2 Å. The holding space is small, so it is difficult for water molecules to break through the linkage between crystal layers to enter it, and the expansion and contraction of the crystal layers are restricted (Khorshidi et al., 2016; Song et al., 2023), which results in the adsorption sites existed on the surface of the minerals mostly. During the adsorption process, DOM combines with the surface charge of kaolin in the form of cationic and water bridges and then adsorbs onto the kaolin sur-face through hydrophobic interaction, hydrogen bonding, and van der Waals forces (Setia et al., 2013). This experiment showed that the crystalline layer spacing and specific surface area did not show large changes after different dry-wet treatments (Table 1), and the adsorption capacity of DOM was not significantly changed. Therefore, due to its high stability and the extremely limited reduction in the number of active adsorption sites triggered by the decrease in specific surface area after different dry-wet treatments, the adsorption process and characteristics of kaolin on two kinds of DOM did not change significantly after different dry-wet treatments (Figure 1, Figure 3).

3.5. Effect of dry-wet alternation on DOM adsorption by illite

There are more potassium ions between the crystal layers of illite (Ibarrola et al., 2012); the linkage of the crystal layers is mainly done through van der Waals bonding, the linkage force is weak, and the crystal structure is unstable, coupled with the strong hydrophilicity, so that the water molecules can enter and hold up the crystal layers through the hydration of the interlayer K^+, resulting in irreversible expansion of the crystal layers. In this experiment, ilmenite showed a lesser increase in the crystal layer spacing after dry-wet treatment (Table 1), which is consistent with the findings of Karaborni (Karaborni et al., 1996). Theoretically, the crystal layer spacing becomes larger, which is more favourable for DOM adsorption. Still, due to the limitation of molecular particle size, it is difficult for the two kinds of DOM to enter the interlayer to affect the adsorption process. Kai Wei and other experiments found that the adsorption of lysine by illite was mainly accomplished through cationic bond bridging (Wei et al., 2018), hydrophobic interaction, and hydrogen bonding, which was manifested as surface adsorption, and belonged to the unstable physical interlayer adsorption very little. Among the many factors affecting the adsorption of DOM by clay minerals, the size of the specific surface area plays a key role. It has a significant effect on the adsorption amount and adsorption strength (Wang et al., 2017). This experiment showed that with the increase in the number of dry-wet treatments, the specific surface area of illite decreased, resulting in a decrease in the active adsorption sites on the mineral surface, reducing the adsorption capacity of DOM, showing a regular change in the saturated adsorption amount of CK>DW1>DW3>DW6 (Table 1, Fig. 1, Fig. 3).

3.6. Effect of dry-wet alternation on DOM adsorption by hematite

Iron oxide has a high specific surface area and active adsorption sites (Wagai & Mayer, 2007). Liu Zichao et al. found that the adsorption of levofloxacin LEV on iron oxides was not only related to the morphology of LEV in solution but also affected by the specific sur-face area and surface charge of iron oxides (Liu et al., 2023), in which the particular surface area plays a greater role in influencing adsorption (Mikutta et al., 2007). After the first dry-wet treatment, the hematite specific surface area showed a relatively significant decrease from 30.7 m^2/g to 30.4 m^2/g, which led to a decrease in the active adsorption sites and a certain magnitude of saturation adsorption. However, with the increase in the number of dry-wet treatments, the specific surface area was relatively stable. The saturated adsorption amount of DOM molecules changed relatively little, which may be attributed to the fact that the first drying and wetting brought it into a relatively more stable characterization state (Table 1, Fig. 1, Fig. 3). Wang Yingying et al. also found through their tests that the shrinkage and deformation of red clay tend to stabilize with the number of dry-wet cycles, which is consistent with the results of this test for hematite (Wang et al., 2014).

3.7. Adsorption behaviour of different minerals on DOM

Kinetic parameters are important indicators of adsorption-desorption characteristics, and related work has been carried out by some researchers. Comparison was found (Table 6) that the parameters of Q_e(exp), K and q_e(cal) of the kinetic process of organic carbon adsorption among different minerals showed large differences. The variation of Q_e(exp) ranged from 1.77-181.60 mg/g, which reflected the contribution of different minerals to the adsorption of organic carbon to a certain extent. However, it should be pointed out that the results of the current related studies are not only affected by the type of minerals supplied for testing, but also by the test conditions such as temperature, carbon adsorbent type and concentration, and the variability among the parameters is the result of the joint action of multiple

Table 6. Kinetic parameters of organic carbon adsorption by different minerals

Mineral type	Q_e(exp) (mg/g)	Pseudo-second-order kinetic model	
		K [g/(mg·min)]	q_e(cal) (mg/g)
Kaolin (Table 2)	11.764	0.593	11.597
Illite (Table 2)	11.432	0.106	11.966
Hematite (Table 2)	2.0210	0.329	1.645
Fe_3O_4@ SiO_2-NH_2 (Wang et al., 2013)	72.030	0.002	71.940
Fe_3O_4@ SiO_2 (Wang et al., 2013)	25.460	− 0.002	6.330
SiO_2 (Wang et al. 2013)	11.080	0.019	11.980
Fluorite (Tangarfa & Hassani, N.S.A., 2022)	1.770	0.12	2.09
Calcite (Tangarfa et al., 2019)	7.890	0.190	8.110
Coal Fly Ash (Li et al., 2013)	4.888	0.007	4.474
Organic montmorillonite (Zhou et al., 2014)	181.600	0.010	195.300
UiO-66 (Zeng et al., 2018)	24.700	0.400	23.300

factors. Therefore, if the contribution of different minerals in the carbon adsorption and desorption process is judged more accurately, more detailed studies are needed in the future.

The results of this study (Table 2, Table 4) show that the Q_e(exp) in the proposed secondary kinetic parameters are closer to the q_e(cal) and have higher R^2. It reflects that kaolin, illite and hematite have the same adsorption characteristics for glucose and tannic acid, which show a covalent bond-linked chemisorption process. Although the previous studies were accomplished under different minerals and different experimental conditions, further comparisons revealed that the results of each study reflected that the fitting effect of the proposed second-order kinetic model was more in line with the kinetic adsorption process (Table 6), implying that chemical adsorption through covalent bonding connection has a very important role in the process of mineral adsorption of organic carbon.

4. Conclusions

(1) The alternation of dry-wet has a small effect on the specific surface area of kaolinite, and the average pore size appears to change irregularly. With the increase in the number of dry-wet times, illite showed a decrease in the specific surface area and an increase in the average pore diameter; the first dry-wet alternation had a greater effect on the specific surface area and average pore diameter of hematite and then tended to stabilize. The dry-wet alternation did not change the spacing between the crystal layers of the three minerals.

(2) The dry-wet alternation did not change the adsorption characteristics of the three minerals on tannic acid and glucose, and the adsorption process was mainly accomplished through surface diffusion, and mesopore diffusion to complete the three phases of rapid adsorption, slow adsorption, and equilibrium adsorption. However, the dry-wet alternation could change the equilibrium adsorption number of tannins and glucose of the three minerals to different degrees, which affected the adsorption capacity of the minerals on tannins and glucose.

(3) Dry-wet alternation did not change the adsorption mode of the three minerals on tannins and glucose. The adsorption behaviours of tannic acid on illite and hematite were monolayer adsorption. In contrast, the adsorption behaviours of tannic acid on kaolinite and glucose on the three minerals were characterized by multilayer adsorption.

(4) The adsorption capacity of kaolinite is less affected by dry-wet alternation due to its high stability and the limited reduction in the number of active sites triggered by the decrease in specific surface area; illite is structurally unstable, its specific surface area is more affected by dry-wet alternation, and its adsorption capacity shows a gradual decrease with the increase in the number of dry-wet times; the first dry-wet alternation obviously reduces the specific surface area of hematite, decreases the number of active adsorption sites, and alters the adsorption The first dry-wet alternation obviously reduced the specific surface area of hematite, decreased the number of active adsorption sites, and changed the adsorption capacity. Still, after that, the in-fluence of dry-wet alternation was not strong, and the adsorption capacity entered a relatively more stable state. The average pore size and crystal layer spacing are not the main limiting factors for the adsorption of tannins and glucose by the three minerals due to the limitation of the particle size of tannins and glucose and the spacing of crystal layers.

Acknowledgments

This work was supported by the financial support from the Ordos City Science and Technology Cooperation Major Special Project (Grant No. 2021EEDSCXQDFZ012).

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