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Tetracycline adsorption by clay under the coexistence of three extracts from an invasive plant

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ABSTRACT

The remediation of contaminated soil by invasive plant resources is a new research hotspot. Different proportions (0%, 1%, 2%, 5%, and 10%) of exudates (E) from the living roots (LR-E), dead roots (DR-E), and fallen leaves (FL-E) of the invasive plant *Alternanthera philoxeroides* were added to a tetracycline (TC) adsorption system to study the influence of extracts from invasive plant roots and litter (fallen leaves and dead roots) on the adsorption of TC by clays (bentonite [B] and kaolin [K]). Then, the batch method was used to study the isotherm adsorption characteristics of TC, and the effects of temperature, pH, and ionic strength on TC adsorption were compared. The following results were obtained: (1) The adsorption isotherms of TC on B and K under the coexistence of E were all consistent with the Henry model, and the adsorption amount of TC increased by 1.04–1.81 times after the addition of E. The addition of LR-E had a strong promoting effect on TC adsorption by the two clays. (2) The adsorption amount of TC on each tested clay with the coexistence of E was positively correlated with temperature within the range of 5°C–40°C. Thermodynamic analysis showed that TC adsorption was a spontaneous, endothermic, and entropy-adding reaction. (3) When the pH was changed from 2 to 10, the adsorption amount of TC on clay decreased. The range of this decrement narrowed with the increase in coexisting E. (4) When the ion concentration was changed from 0.01 to 0.5 mol/L, the adsorption amount of TC on B decreased with the increase in ionic strength, whereas that on K first increased and then decreased. In conclusion, invasive plant extracts can improve the adsorption of TC on clay, and the adsorption effect is superior when the temperature is high and the pH is low.

Keywords: Tetracycline; Clay; Invasive plant; Extract; Adsorption amount

1. Introduction

In recent years, tetracycline (TC) has become the most widely used antibiotic in the breeding industry due to its high quality, low price, and broad-spectrum resistance [1]. Given that animals cannot fully absorb TC, 25%–90% of TC enters the environment in the prototype or metabolite form. The long-term use of manure has resulted in the accumulation of large amounts of TC in the soil, thus resulting in severe soil pollution [2–4]. Therefore, research on the removal of TC from the soil has vital importance for the soil environment.

At present, the main methods for removing TC from the soil include adsorption and fixation [5–7], biodegradation

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[8,9], and photocatalytic degradation [10]. Among these methods, adsorption and fixation are widely used due to their good economy and high efficiency. Wang et al. [11] found that the adsorption process of TC and oxytetracycline on clay, loam and sand can be divided into the fast adsorption stage and the slow equilibrium stage. This adsorption behavior can be described by the Freundlich model with an average coefficient of 0.996. Loam has the strongest adsorption capacity for TC and oxytetracycline, and sand has the weakest adsorption capacity [12]. TC desorption exhibits hysteresis in Cu-contaminated soil, and the hysteresis coefficient of TC in wet and black soil gradually decreases with the increase in soil Cu concentration [13]. Zhang et al. [14] studied the adsorption of TC by clay minerals by liquid chromatography and spectrophotometry and found that the hydroxyl functional group of TC plays an important role in adsorption. The hydroxyl functional group has been proven to promote adsorption for the first time via infrared spectroscopy and thermogravimetric analysis. The best strengthening effect of bentonite (B) is achieved when the addition amounts of B, diatomite, and active calcium silicate are consistent, the strengthening effect of bentonite is the best. An increase in temperature is beneficial for the adsorption of TC in various types of soil samples [15]. Studies have also found that the adsorption of TC by cetyltrimethylammonium bromide-modified attapulgite clay conforms to the quasi-second-order kinetic model, and the adsorption isotherm of this process conforms well to the Langmuir isotherm. The enhanced hydrophobicity of organically modified attapulgite clay improves the adsorption capacity of organic pollutants [16]. Wang et al. [17] used the amphoteric surfactant octadecyl dimethyl betaine (BS-18) to modify B and found that the adsorption of TC by BS-18-modified B is mainly based on the charge and is positively affected by increasing temperatures.

"Plant root extract" is a general term for organic matter released from roots into the rhizosphere environment under certain growth conditions [18]. Plant root extracts can absorb or degrade heavy metals and organic compounds in the environment by adjusting the rhizosphere pH, forming chelates with heavy metals, increasing the number of microorganisms, and secreting enzymes [19]. Yang et al. [20] found that root extracts (organic acids and amino acids) have a strong activation effect on heavy metal elements (Pb, Zn, Cd, and Cu) in the soil. Among these extracts, citric acid, tartaric acid, and oxalic acid have the strongest activation capacity. Ryegrass root extracts affect on the bioavailability and migration transformation of heavy metals in clay zinc refinery waste, and the addition of amino acids and organic acids improves the bioavailability of heavy metal elements (Cu, Zn, and Cd) [21]. Plant litter is an important resource in the carbon and nutrient cycling of terrestrial ecosystems, and its decomposition has great importance for the formation of soil organic matter and the release of nutrients [22]. Studies have shown that in fir plantation ecosystems, the litter of some associated plant species interacts with each other in the process of mixed decomposition, which is important for accelerating nutrient cycling [23]. Rao et al. [24] Investigated decomposition in a wetland system by adding different amounts of *Broussonetia papyrifera* litter and found that the input of *B. papyrifera* as exogenous organic matter would promote the leaching of characteristic pollutants, such as Fe and Mn, from sediment. The decomposition of the fallen leaves of *Autumn eggplant* and *Avicennia marina* exerted different degrees of adsorption and accumulation effects on nine metal elements. The proportion of elements in the decomposition groups of *A. eggplant* on the beach surface and in sediment during winter changed from high to low as follows: Pb > Fe > Cd > Cr > Ag > Ni > Cu > Zn and Pb > Cd > Cr > Fe > Ag > Ni > Cu [25].

Studies on plant roots and litter extracts mainly focused on activating heavy metals in the soil and promoting nutrient cycling in plants. Further investigations on the effect of plant extracts on antibiotic contamination in the soil are needed. Invasive plants are harmful, fast-growing, and highly adaptable species. The effect of extracts from invasive plants on antibiotic contamination in the soil has rarely been studied. In this study, B and kaolin (K) were used as soil samples, and *Alternanthera philoxeroides* was used as an invasive plant. The isothermal adsorption of TC by clays under the coexistence of extracts were studied, and the differences in adsorption under different environmental conditions such as temperature, pH, and ion concentration, were compared to provide a reference for the application of invasive plants in pollution remediation.

2. Materials and methods

2.1. Experimental materials

A. philoxeroides was selected as the invasive plant and was obtained from the experimental field of China West Normal University, Sichuan Province, China. TC was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The purity of TC was 99.9%. B and K were purchased from Kelong Chemical Reagent Factory of Chengdu. The two clays were purified via the water-washing method before use [15]. The basic physicochemical properties and surface morphology of the tested clays are shown in Table 1 and Fig. 1, respectively.

2.2. Experimental design

2.2.1. Collection of root and litter exudates

The living roots (LR), dead roots (DR), and fallen leaves (FL) of *A. philoxeroides* were crushed separately, then mixed with distilled water at a mass ratio of 1:20 (biomass:water), shaken for 2 h, and centrifuged for separation at 4,800 rpm for 20 min. The different exudates (Es) were designated as LR-E, FL-E, and DR-E and placed in a refrigerator at 4°C for later use. The basic physicochemical properties of the tested Es are shown in Table 2.

Table 1
Basic physicochemical properties of the test materials

Clays	B	K
pH	10.21	7.02
CEC (mmol/kg)	1,001.25	85.24
Specific surface area (m^2/g)	62.88	10.43
Interlayer spacing (nm)	1.44	0.70

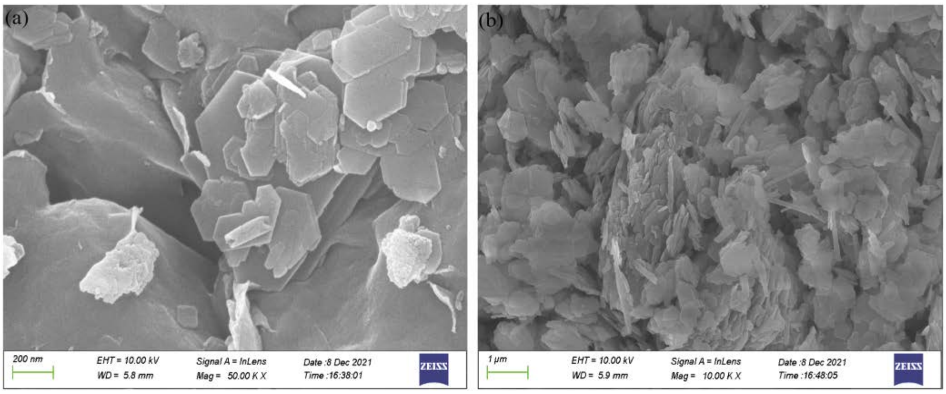

Fig. 1. Surface morphology of B (a) and K (b).

Table 2
Basic physicochemical properties of test Es

Exudates	Dissolved organic carbon (mg/L)	A(335)	$SUVA_{254}$	$SUVA_{260}$
LR-E	183.58	19.11	5.75	5.59
DR-E	264.23	20.73	2.62	2.59
FL-E	432.36	37.31	1.64	1.60

Note: A(335) represents the relative concentration of colored dissolved organic matter (DOM). A high A(335) value is indicative of the high relative concentration of colored DOM. $SUVA_{254}$ is the aromaticity strength of DOM, and a high $SUVA_{254}$ is indicative of high aromaticity. $SUVA_{260}$ is the hydrophobic component of DOM, and a high $SUVA_{260}$ value is indicative of high hydrophobic component content.

2.2.2. Setting of the coexistence ratio of E

LR-E, DR-E, and FL-E were uniformly added into the solution system (TC absorbed by clay) at a certain mass ratio (0%, 1%, 2%, 5%, and 10%), and then the experiment on TC adsorption by B and K was carried out. Different treatments were expressed as $B_{(0–10\%)LR-E}$ (TC adsorbed by B with the coexistence of E, the same as below), $K_{(0–10\%)LR-E}$, $B_{(0–10\%)DR-E}$, $K_{(0–10\%)\%DR-E}$, $B_{(0–10\%)FL-E}$, and $K_{(0–10\%)FL-E}$.

2.2.3. Isothermal adsorption experiment for TC

A total of nine TC concentration gradients were set as 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 mg/L. At this time, the experimental conditions were as follows: the temperature was 25°C, pH value of TC solution was 7, and ionic strength was 0.1 mol/L.

2.2.4. Influencing factor experiment

Temperature, pH and ionic strength were considered as the environmental influencing factors. Temperature is set at 10°C, 20°C, 30°C and 40°C (pH value of the solution: 7; ionic strength: 0.1 mol/L). pH values are set at 2, 4, 6, 8, 10 (initial solution temperature: 30°C; ionic strength: 0.1 mol/L). Ionic strength was set at 0.01, 0.05, 0.1, 0.2 and 0.5 mol/L (pH value of the solution: 7; initial solution temperature: 30°C).

2.3. Experimental methods

A total of 0.2000 g of different clays was accurately weighed into nine 50 mL polyacrylamide centrifuge tubes, and 20 mL of the above TC series solution was successively added. Then the corresponding E was added in accordance with the volume of the TC solution. The samples were oscillated at 150 rpm and the constant temperature of 20°C for 12 h. After centrifugation at 4,800 rpm for 15 min, the supernatant was separated through a 0.45 μm filter membrane, and the TC adsorption capacity of each tested clay was calculated through the difference subtraction method. The above experiments were repeated under different influencing factors to compare the differences in TC adsorption. TC concentration was determined via liquid chromatography.

2.4. Data processing

2.4.1. Calculation of equilibrium adsorption capacity

Equilibrium adsorption capacity was calculated according to Eq. (1).

$$q = \frac{\left(C_0 - C_e\right)V}{m} \tag{1}$$

where C_0 and C_e are the initial concentration and equilibrium concentration of TC in solution, respectively (mmol/L). V refers the volume of TC solution added (mL). m is the mass of the tested clay sample (g). q indicates the equilibrium adsorption capacity of TC on the tested clay sample.

2.4.2. Fitting of adsorption isotherms

Henry model was used to fit the adsorption isotherm of TC, as shown in Eq. (2).

Table 3
Fitting parameters of the TC adsorption isotherms by the Henry model

Treatments	Correlation coefficient (r)	Equilibrium constant (K)	Standard error (S)
$B_{0\%\text{LR-E}}$	0.9928**	57.71	0.18
$B_{1\%\text{LR-E}}$	0.9961**	109.28	0.19
$B_{2\%\text{LR-E}}$	0.9877**	98.75	0.34
$B_{5\%\text{LR-E}}$	0.9928**	118.00	0.27
$B_{10\%\text{LR-E}}$	0.9778**	141.09	0.49
$K_{0\%\text{LR-E}}$	0.9602**	39.68	0.36
$K_{1\%\text{LR-E}}$	0.9879**	62.88	0.25
$K_{2\%\text{LR-E}}$	0.9867**	61.95	0.27
$K_{5\%\text{LR-E}}$	0.9920**	72.79	0.21
$K_{10\%\text{LR-E}}$	0.9914**	108.17	0.26
$B_{0\%\text{DR-E}}$	0.9766**	53.89	0.32
$B_{1\%\text{DR-E}}$	0.9825**	52.27	0.26
$B_{2\%\text{DR-E}}$	0.9788**	60.98	0.33
$B_{5\%\text{DR-E}}$	0.9816**	58.67	0.29
$B_{10\%\text{DR-E}}$	0.9917**	49.23	0.17
$K_{0\%\text{DR-E}}$	0.9872**	62.71	0.25
$K_{1\%\text{DR-E}}$	0.9913**	55.82	0.19
$K_{2\%\text{DR-E}}$	0.9593**	55.98	0.47
$K_{5\%\text{DR-E}}$	0.9788**	53.48	0.29
$K_{10\%\text{DR-E}}$	0.9832**	49.88	0.26
$B_{0\%\text{LF-E}}$	0.9445**	39.57	0.41
$B_{1\%\text{LF-E}}$	0.9737**	85.42	0.44
$B_{2\%\text{LF-E}}$	0.9704**	62.12	0.38
$B_{5\%\text{LF-E}}$	0.9766**	101.24	0.46
$B_{10\%\text{LF-E}}$	0.9689**	111.54	0.56
$K_{0\%\text{LF-E}}$	0.9744**	37.10	0.27
$K_{1\%\text{LF-E}}$	0.9808**	97.03	0.39
$K_{2\%\text{LF-E}}$	0.9796**	59.62	0.33
$K_{5\%\text{LF-E}}$	0.9721**	98.59	0.47
$K_{10\%\text{LF-E}}$	0.9753**	111.89	0.49

Note: **indicates significance at the $p = 0.01$ level ($r = 0.765$ at $p = 0.01$ when the degrees of freedom $f = 8$).

$$S = KC \tag{2}$$

where S is the equilibrium adsorption amount of TC adsorbed by clay samples (mmol/kg); C is the equilibrium concentration of TC in the supernatant (mmol/L); K represents the distribution coefficient of TC in solid phase adsorbent and solvent, and also represents the TC binding capacity of the tested clay sample to a certain extent.

2.4.3. Calculation of thermodynamic parameters

The parameter K in Henry model is the apparent adsorption constant equivalent to the equilibrium constant, then $K = K_a$. The thermodynamic parameters calculated by K_a are called the apparent thermodynamic parameters [26], and the calculation formulas are shown in Eqs. (3)–(5).

$$\Delta G = -RT\ln K \tag{3}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

$$\Delta H = R\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right) \cdot \ln\left(\frac{K_a, T_2}{K_a, T_1}\right) \tag{5}$$

where ΔG is the standard free energy change (kJ/mol); R is constant (8.3145 J/mol K); T is the adsorption temperature (T_1 = 293.16 K, T_2 = 313.6 K); ΔH is the enthalpy change of adsorption process (kJ/mol); ΔS is the entropy change of adsorption process (J/mol K).

Curvexpert1.4 fitting software was used to fit the adsorption isotherm by the stepwise approximation method. SPSS 16.0 statistical analysis software was used to process the experimental data for variance and correlation analysis. SigmaPlot 10.0 software was adopted to improve data plotting. The data were expressed as the means with standard deviation, and different letters indicate significant differences among various amendments. Analysis of variance was performed to determine the effects of amendments, followed by Tukey's honestly significant difference test. Differences of $p < 0.05$ were considered significant.

3. Results and discussion

3.1. TC adsorption isotherm of clay with the coexistence of E

The adsorption isotherms of TC under each treatment are shown in Fig. 2. Under the conditions of 20°C, pH = 7, and ionic strength of 0.1 mol/L, the adsorption amount of TC under each treatment increased with the increase in equilibrium concentration. The adsorption isotherms all presented a linear adsorption type, proving that the Henry model was appropriate for describing the adsorption of TC by B and K. Table 3 shows the fitting results of the adsorption isotherms via the Henry model.

The TC adsorption capacity on the two clays with the coexistence of E all increased relative to that on the original clay sample without E. The adsorption capacities of TC on the two clays with the coexistence of LR-E followed the order of $B_{10\%\text{LR-E}} > B_{5\%\text{LR-E}} > B_{1\%\text{LR-E}} > B_{2\%\text{LR-E}} > B_{0\%\text{LR-E}}$ and $K_{10\%\text{LR-E}} > K_{5\%\text{LR-E}} > K_{1\%\text{LR-E}} > K_{2\%\text{LR-E}} > K_{0\%\text{LR-E}}$. Therefore, the high concentration of LR-E was associated with the high adsorption capacity for TC. This result was consistent with Li's findings, which showed a significant positive correlation between soil organic matter and TC adsorption capacity [27]. The TC adsorption capacity on B was diminished by the addition of 1% and 10% DR-E and enhanced by the addition of 2% and 5% DR-E. The TC adsorption capacity on K lessened with the coexistence of different proportions of DR-E. The coexistence of different proportions of FL-E increased the TC adsorption capacity on B and K. The adsorption capacities for TC followed the order of $B_{10\%\text{FL-E}} > B_{5\%\text{FL-E}} > B_{1\%\text{FL-E}} > B_{2\%\text{FL-E}} > B_{2\%\text{FL-E}}$ and $K_{10\%\text{FL-S}} > K_{5\%\text{FL-S}} > K_{1\%\text{FL-S}} > K_{2\%\text{FL-S}} > K_{0\%\text{FL-E}}$. The results of TC adsorption on the two clays with the coexistence of FL-E was consistent with those on the two clays with the coexistence of LR-E. The

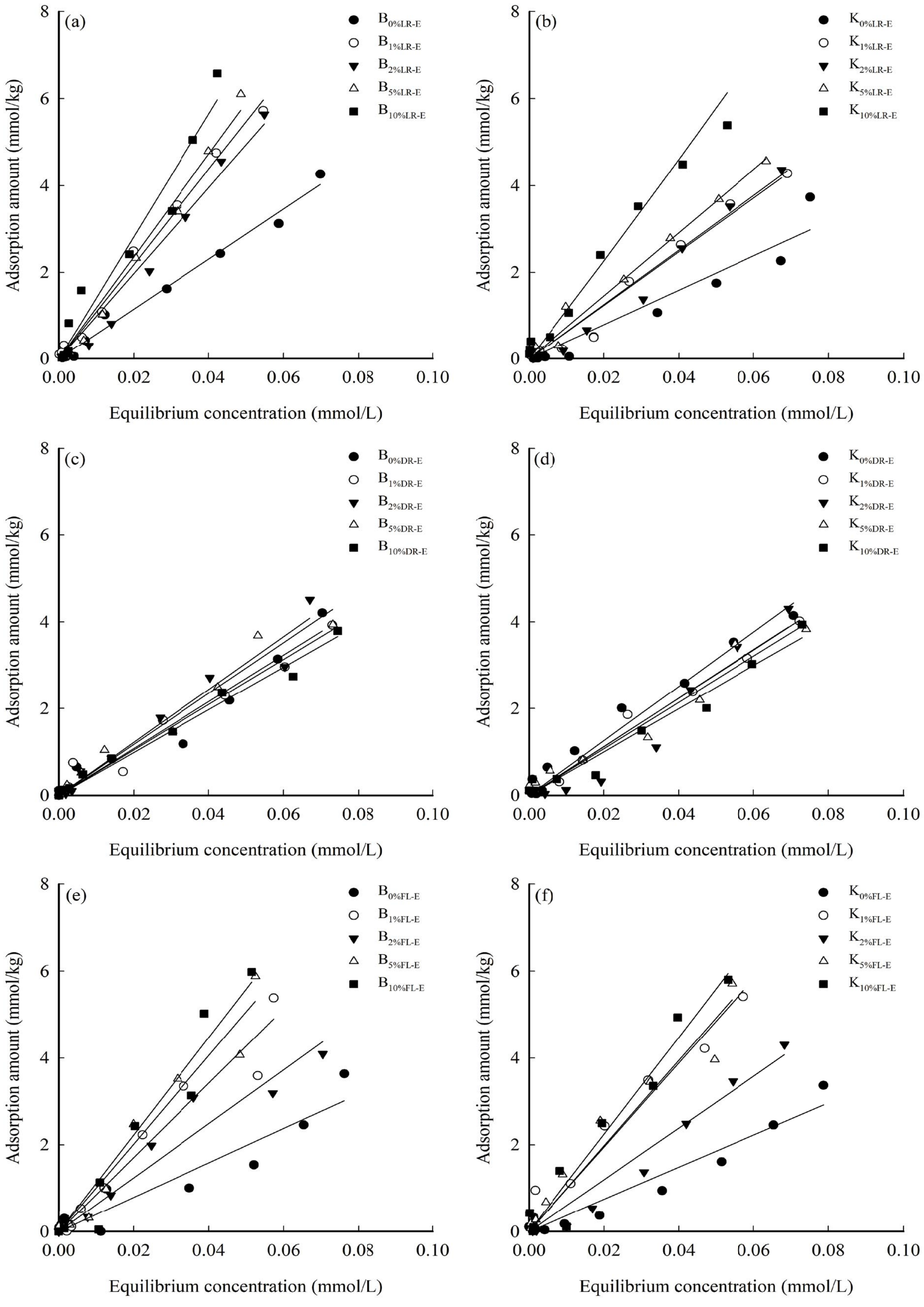

Fig. 2. Adsorption isotherms of TC under different treatments.

adsorption capacities for TC on B were ranked in the order of $B_{LR-E} > B_{FL-E} > B_{DR-E}$. The TC adsorption capacities on K followed the order of $K_{FL-E} > K_{LR-E} > K_{DR-E}$. Therefore, coexistence with LR-E and FL-E can maximally promote the adsorption of TC on B and K, respectively.

3.2. Influence of temperature on TC adsorption by clay coexisting with E

At pH = 7 and ionic strength = 0.01 mol/L, the TC adsorption amounts under different treatments all increased with the increase in temperature, showing that temperature had a positive effect (Fig. 3). When the temperature was changed from 5°C to 40°C, the TC adsorption under different treatments were increased by 55.78%–107.16%. The range of increase in TC adsorption followed the order of $B_{LR-E} > B_{FL-E} > B_{DR-E}$ and $K_{FL-E} > K_{LR-E} > K_{DR-E}$. With the increase in coexisting E, the range of the increase in TC adsorption broadened. The above results were the same as those for the adsorption isotherm in Fig. 1 and similar to the results of TC adsorption on modified clay reported by Zou et al. [28].

The Henry model was used to fit the isotherm of TC adsorption under the tested treatments (Table 4). Under the conditions of 5°C and 40°C, the apparent free energy (ΔG) of TC adsorption was less than 0, indicating that the adsorption process was spontaneous and that the spontaneous process at 40°C was stronger than that at 5°C. The apparent enthalpy of TC adsorption was $\Delta H > 0$, and the apparent entropy change was $\Delta S > 0$, showing that the reaction was endothermic and entropy-increasing. Therefore, increasing the temperature was conducive to TC adsorption. This conclusion mutually verified the above conclusion regarding the effect of temperature.

3.3. Influence of pH and ionic strength on TC adsorption

The effects of pH on TC adsorption at the temperature of 20°C and the ionic strength of 0.1 mol/L are shown in Table 5. With the increase in pH, the adsorption amount of TC under different treatments decreased. Under different B treatments, TC adsorption (affected by the increase in pH) decreased within the range of 51.24%–91.96% and followed the trend of $B_{FL-E} > B_{LR-E} > B_{DR-E}$. The range of the decrease in TC adsorption on K under different treatments was 58.80%–95.41% and followed the trend of $K_{FL-E} \approx K_{LR-E} > K_{DR-E}$. The range of reduction narrowed under all treatments with the increase in coexisting E. Consistent with the above conclusion, soil pH has be found to be capable of affecting the existing form of TC in solution [29].

At pH = 3 and 20°C, the adsorption amount of TC on B under each treatment decreased within the range of 55.12% to 93.21% with the increase in ionic strength within the range of 0.01–0.5 mol/L (Fig. 4). The adsorption amount of TC on K first increased and then decreased with the increase in ionic strength and stayed at the maximum value at 0.05 mol/L. The range of decrease in TC adsorption under different treatments was 58.80%–95.41% and followed the trend of $B_{DR-E} > B_{FL-E} > B_{LR-E}$ and $K_{DR-E} > K_{FL-E} > K_{LR-E}$. The range of decrease in the amount of TC adsorption amount on the two clays all broadened with the increase in coexisting E.

3.4. Mechanism underlying the effect of the coexistence of E on TC adsorption

The TC adsorption process on clay samples coexisting with E is illustrated in Fig. 5. The absorption of TC by natural clay depended on the physical and chemical properties

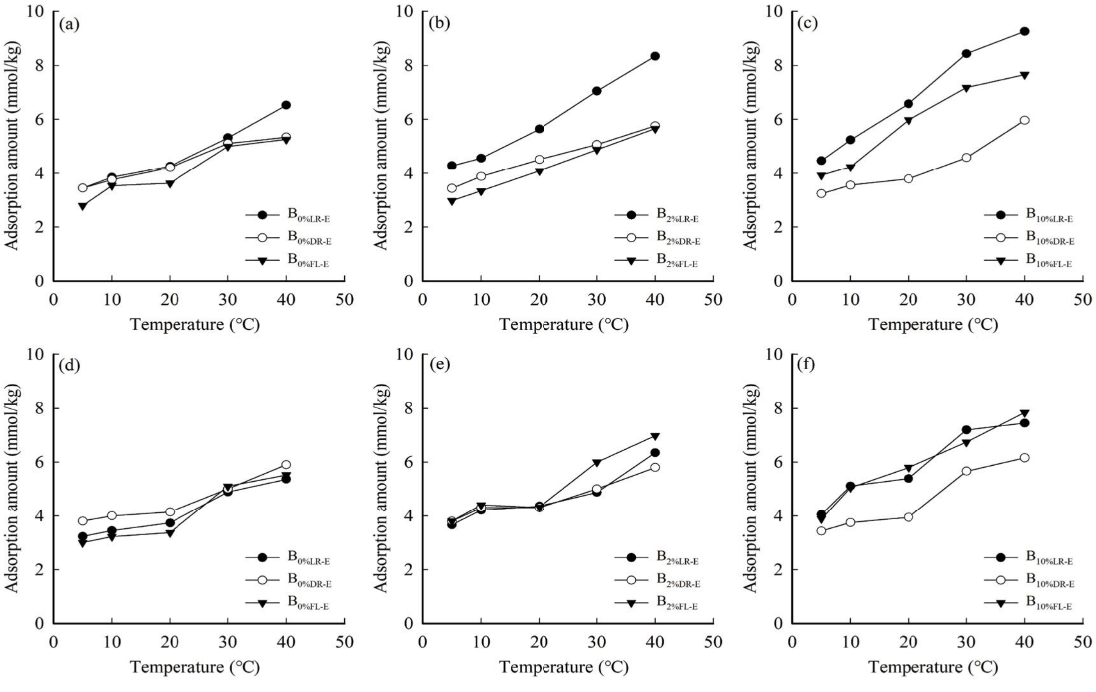

Fig. 3. TC adsorption under each treatment at different temperatures.

Table 4
Thermodynamic parameters of TC adsorption under different treatments

Treatments	5°C			40°C		
	Δ*G* (kJ/mol)	Δ*H* (kJ/mol)	Δ*S* (J/mol K)	Δ*G* (kJ/mol)	Δ*H* (kJ/mol)	Δ*S* (J/mol K)
$\mathrm{B}_{0\%\mathrm{LR-E}}$	–8.89	13.20	79.43	–11.67	13.20	79.43
$\mathrm{B}_{2\%\mathrm{LR-E}}$	–9.98	13.80	85.52	–12.98	13.80	85.52
$\mathrm{B}_{10\%\mathrm{LR-E}}$	–10.55	15.07	92.11	–13.78	15.07	92.11
$\mathrm{B}_{0\%\mathrm{DR-E}}$	–8.76	9.04	63.99	–11.00	9.04	63.99
$\mathrm{B}_{2\%\mathrm{DR-E}}$	–8.88	10.67	70.26	–11.34	10.67	70.26
$\mathrm{B}_{10\%\mathrm{DR-E}}$	–8.65	12.65	76.55	–11.33	12.65	76.55
$\mathrm{B}_{0\%\mathrm{LF-E}}$	–7.90	13.12	75.56	–10.54	13.12	75.56
$\mathrm{B}_{2\%\mathrm{LF-E}}$	–8.82	13.27	79.42	–11.60	13.27	79.42
$\mathrm{B}_{10\%\mathrm{LF-E}}$	–9.93	13.81	85.35	–12.92	13.81	85.35
$\mathrm{K}_{0\%\mathrm{LR-E}}$	–8.18	10.48	67.08	–10.53	10.48	67.08
$\mathrm{K}_{2\%\mathrm{LR-E}}$	–9.14	11.40	73.84	–11.72	11.40	73.84
$\mathrm{K}_{10\%\mathrm{LR-E}}$	–10.17	12.61	81.91	–13.04	12.61	81.91
$\mathrm{K}_{0\%\mathrm{DR-E}}$	–9.37	9.10	66.41	–11.69	9.10	66.41
$\mathrm{K}_{2\%\mathrm{DR-E}}$	–9.02	8.75	63.88	–11.26	8.75	63.88
$\mathrm{K}_{10\%\mathrm{DR-E}}$	–8.72	12.11	74.91	–11.34	12.11	74.91
$\mathrm{K}_{0\%\mathrm{LF-E}}$	–8.09	12.62	74.45	–10.70	12.62	74.45
$\mathrm{K}_{2\%\mathrm{LF-E}}$	–9.16	12.58	78.18	–11.90	12.58	78.18
$\mathrm{K}_{10\%\mathrm{LF-E}}$	–9.98	14.55	88.20	–13.07	14.55	88.20

Table 5
Effect of pH on TC adsorption under different treatments

Treatments	Adsorption amount of TC (mmol/kg)				
	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
$\mathrm{B}_{0\%\mathrm{LR-E}}$	6.75 ± 0.12a	5.60 ± 0.06b	4.56 ± 0.09c	4.34 ± 0.20c	3.64 ± 0.02d
$\mathrm{B}_{2\%\mathrm{LR-E}}$	7.24 ± 0.14a	5.96 ± 0.02b	5.84 ± 0.20b	5.44 ± 0.12b	4.12 ± 0.07c
$\mathrm{B}_{10\%\mathrm{LR-E}}$	7.88 ± 0.17a	7.55 ± 0.14a	6.78 ± 0.16b	5.24 ± 0.14c	4.86 ± 0.18c
$\mathrm{B}_{0\%\mathrm{DR-E}}$	6.47 ± 0.16a	5.13 ± 0.08b	4.41 ± 0.24c	4.18 ± 0.10c	3.37 ± 0.04d
$\mathrm{B}_{2\%\mathrm{DR-E}}$	6.55 ± 0.26a	5.56 ± 0.03b	4.81 ± 0.17c	4.31 ± 0.01cd	3.75 ± 0.14d
$\mathrm{B}_{10\%\mathrm{DR-E}}$	6.75 ± 0.09a	5.33 ± 0.19b	4.39 ± 0.23c	4.22 ± 0.13c	4.04 ± 0.03c
$\mathrm{B}_{0\%\mathrm{LF-E}}$	6.23 ± 0.13a	4.83 ± 0.19b	3.93 ± 0.02c	3.36 ± 0.15cd	3.14 ± 0.08d
$\mathrm{B}_{2\%\mathrm{LF-E}}$	6.69 ± 0.12a	5.67 ± 0.10b	4.69 ± 0.05c	4.25 ± 0.14c	3.11 ± 0.06d
$\mathrm{B}_{10\%\mathrm{LF-E}}$	7.42 ± 0.24a	7.25 ± 0.14a	6.28 ± 0.16b	5.66 ± 0.09b	4.52 ± 0.11c
$\mathrm{K}_{0\%\mathrm{LR-E}}$	6.03 ± 0.02a	4.65 ± 0.09b	3.93 ± 0.13c	3.56 ± 0.03d	3.12 ± 0.07e
$\mathrm{K}_{2\%\mathrm{LR-E}}$	6.52 ± 0.18a	5.14 ± 0.08b	4.56 ± 0.03c	4.14 ± 0.08c	3.58 ± 0.10d
$\mathrm{K}_{10\%\mathrm{LR-E}}$	6.86 ± 0.15a	6.45 ± 0.26a	5.49 ± 0.12b	5.00 ± 0.06bc	4.32 ± 0.18c
$\mathrm{K}_{0\%\mathrm{DR-E}}$	5.95 ± 0.03a	5.14 ± 0.08b	4.34 ± 0.20c	3.96 ± 0.02c	3.35 ± 0.12d
$\mathrm{K}_{2\%\mathrm{DR-E}}$	6.02 ± 0.01a	4.96 ± 0.06b	4.50 ± 0.12c	4.05 ± 0.03d	3.38 ± 0.10e
$\mathrm{K}_{10\%\mathrm{DR-E}}$	6.17 ± 0.10a	5.43 ± 0.12b	3.99 ± 0.17c	3.73 ± 0.07c	4.64 ± 0.08c
$\mathrm{K}_{0\%\mathrm{LF-E}}$	5.96 ± 0.12a	4.78 ± 0.05b	3.57 ± 0.10c	3.33 ± 0.19cd	3.05 ± 0.03d
$\mathrm{K}_{2\%\mathrm{LF-E}}$	6.42 ± 0.12a	5.63 ± 0.08b	4.41 ± 0.24c	4.11 ± 0.06c	3.73 ± 0.13d
$\mathrm{K}_{10\%\mathrm{LF-E}}$	7.13 ± 0.08a	6.36 ± 0.21b	5.92 ± 0.05b	5.03 ± 0.02c	4.56 ± 0.03c

Note: The different lowercase letters in the same row indicate significant difference among treatments at $p = 0.05$ level.

of the clay. The adsorption capacity of clay for TC mainly relied on the negative charge adsorption points between layers [12,28]. However, the original clay had low TC adsorption because it had finite adsorption sites. Es from invasive plants were mainly composed of cellulose, hemicellulose, and pectin. Research has demonstrated that the adsorption affinity of Es mainly originate from the surface bonding of cellulose and the complexing action of pectin.

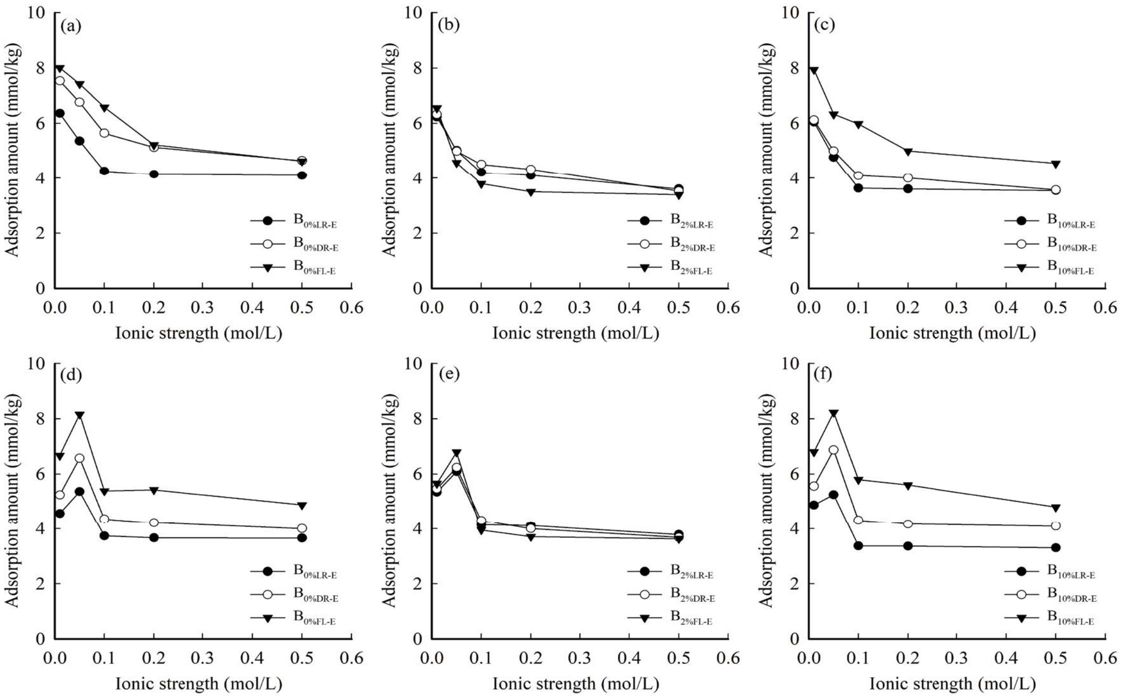

Fig. 4. Adsorption amount of TC at different ionic strengths.

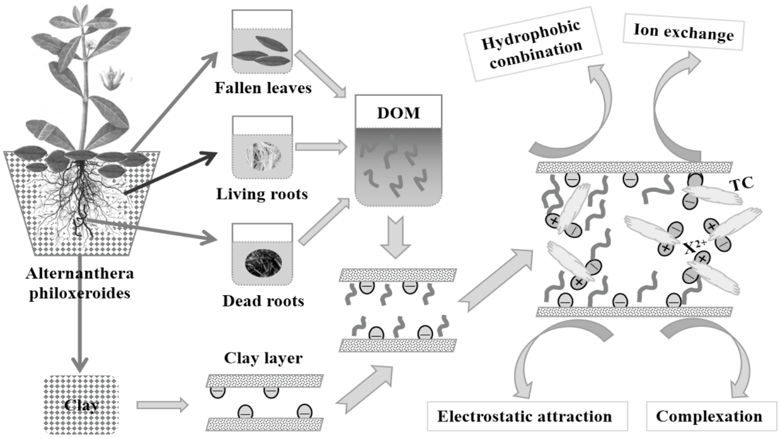

Fig. 5. TC adsorption on clay samples with the coexistence of E.

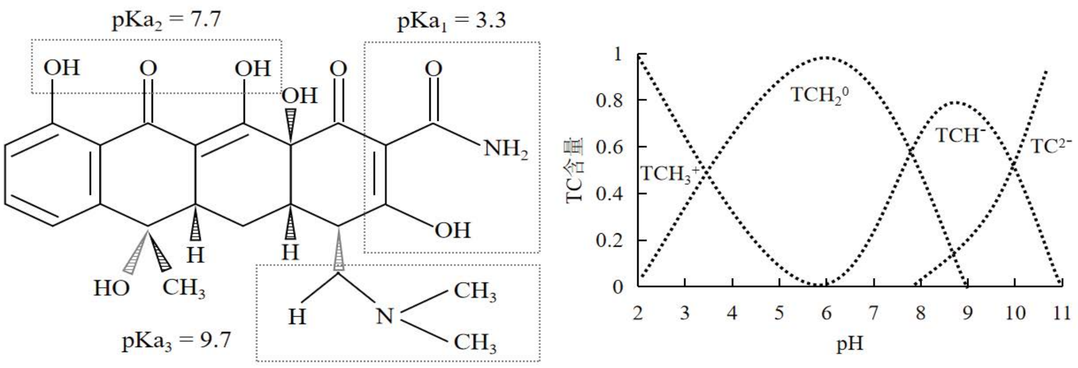

Fig. 6. Structure and pH-dependent speciation of TC.

Therefore, clay coexisting with E had higher TC binding capacity than the original clay. The adsorption mechanism mainly included ion exchange, hydrophobic combination, complexation, and electrostatic attraction.

The structure and pH-dependent speciation of TC are depicted in Fig. 6. The TC molecule contains one basic group and two acidic functional groups and exists in four forms in aqueous solution. Colaizzi and Klink [30] found that when pH < 3.3, TC mainly exists in the form of cations, and when pH > 7.7, TC mainly exists in the form of anions. Given that B and K have numerous exchangeable cations in their interlayers, TC existed in cationic form and can exchange with the ions in the clay interlayer when pH = 2. With the increase in pH, the anion form of TC increased gradually. This effect reduced the exchange energy of clay for TC. The above results for the effect of temperature indicated that TC adsorption was endothermic and that its reaction mechanism was mainly chemical. Cellulose and pectin in Es had strong surface bonding and complexing action with TC. Therefore, ion exchange and complexation were the main mechanism of TC adsorption by clay coexisting with E.

4. Conclusion

- The Henry model was suitable for describing the adsorption of TC by clay with the coexistence of E, and the adsorption amount of TC increased by 1.04–1.81 times after the addition of E.
- TC adsorption by clay with the coexistence of E was positively correlated with temperature and was a spontaneous, endothermic, and entropy-adding reaction.
- When the pH was changed from 2 to 10, the adsorption amount of TC on clay with the coexistence of E decreased, and the range of this decrease narrowed with the increase in coexisting E.
- When the ion concentration was changed from 0.01 to 0.5 mol/L, the adsorption amount of TC on B with the coexistence of E decreased with the increase in ionic strength, whereas it first increased and then decreased on K.

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Compliance with ethical standards

The authors declare that they have no conflict of interest.

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