



Enhancing tetracycline adsorption by riverbank soils by application of biochar-based composite materials

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ABSTRACT

To explore the effect of adding biochar (C)-based composite materials on tetracycline (TC) adsorption by bank soils, bentonite (B) and dodecyl dimethyl betaine (BS)-modified B (BS-B) were separately supported on the pores and surface of C (prepared by xeromorphic (XAp-C) and hydrophytic (HAp-C) *Alternanthera philoxeroides*) to form C-based composite materials. Then, 1% (mass ratio) composite materials were used to amend the bank soil obtained from Mianyang (MY), Suining (SN), and Hechuan (HC) along Fu River. The effects of pH, temperature, and ionic strength on TC adsorption were studied, and the isothermal adsorption characteristics of TC on different amended soils were compared under the best environmental conditions. The results showed the following: (1) at the pH range of 3–6, the adsorption of TC on amended bank soils decreased with the increase in pH. In the range of 10°C–40°C, TC adsorption amount of each amended soil increased with the increase in temperature. With the increase in ionic strength, the adsorption amount of TC by amended soils increased first and then decreased, (2) the adsorption isotherms of TC on each sample were L-shaped and accorded with the Langmuir model. The maximum adsorption capacity (q_m) of TC was 9.33–21.29 mmol/kg. At the same conditions, q_m of TC on different amended soils showed the trend of SN > HC > MY when using XAp-C and with BS-B loading presenting best soil improvement effect, (3) TC adsorption of each amended soil was a spontaneous, endothermic, and entropy-adding process. Cation exchange capacity and total organic carbon of bank soil are the key factors to determining the adsorption effect of TC.

Keywords: Biochar; Amphoteric clay; Riverbank soil; Tetracycline; Adsorption amount

1. Introduction

Antibiotics are widely used in animal and poultry breeding as medical veterinary drugs and mainly added to animal feed to prevent animal diseases and promote the healthy growth of livestock and poultry [1–3]. Antibiotics cannot be completely absorbed and metabolized by animals, and more than 85% are excreted in the form of original drugs or metabolites through animal feces and urine [4–6]. Tetracyclines (TCs) are widely used in livestock

and poultry because of their low price and broad-spectrum antibacterial properties in the aquaculture industry [7]. The content of TC in liquid manure approximates 4.0 mg/kg, and the highest concentration of TC in the soil layer applied with manure reaches 198.7 µg/kg [8], which poses a potential threat to soil environment and biological health. Therefore, how to effectively control the TC pollution in the soil environment has become an important issue for researchers.

Antibiotic pollution repair techniques commonly include chemical oxidation, photocatalysis, ion exchange,

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and adsorption methods [9–11]. Adsorption technology is widely used in the removal of most antibiotics due to its advantages, such as simple operation and superior adsorption effect. Thus, adsorbent is the key to determining the adsorption effect. At present, other adsorbents, including bentonite (B), ion exchange resin, and agricultural and forestry wastes are being studied [12]. Biochar (C) has a strong adsorption capacity for organic pollutants because of its porous structure and rich surface oxygen-containing functional groups [13]. Duan et al. [14] observed that C could improve the adsorption capacity of soil toward antibiotics and reduce the relative abundance of antibiotic resistance genes in soil. Several studies showed that B with high adsorption performance is also widely used in the treatment of TC pollution. Wu et al. [15] reported that B had more advantages than kaolin in the treatment of TC-containing wastewater due to its large specific surface area and strong adsorption capacity. Zhang et al. [2] studied the adsorption characteristics, such as initial dosage, adsorption temperature, and solution pH, and identified the optimal conditions for experimental adsorption of B for TC hydrochloride in aqueous solution under different conditions. The adsorption performance to various pollutants of B modified by amphoteric modifier had greatly improved [16,17]. Chai et al. [18] used cationic surfactant cetyltrimethyl ammonium bromide to modify attapulgite, the hydrophobicity of cation-modified attapulgite was enhanced, which improved the adsorption capacity of TC. Loading of clay minerals on C will improve the high adsorption performance and reduce the cost. Chen et al. [19] recorded the 32.36 mg/g maximum adsorption capacity of modified B by C for Eu(III). C and amphoteric modified B are all cost-effective and environment-friendly, and have high contaminant capture capacity. Thus, C loaded with amphoteric B can be used to adsorb TC in the soil to alleviate and repair polluted soils. At present, the application of C composites is mainly focused on nano-metal-loaded materials, whereas the application of modified clay-loaded C materials is rarely studied.

The development of agricultural and animal husbandry production in northeastern Sichuan has caused serious TC pollution in soil, and the water body of Fu River has been threatened by potential pollution. Riverbank is the last barrier to prevent pollutants from entering rivers. If high-adsorbent materials are added to the riverbank soil, the adsorption and fixation of TC pollution by the bank soil can be enhanced. In this experiment, bank soil samples from Mianyang (MY), Suining (SN), and Hechuan (HC) in Fu River were used as research objects. The effect of adding C-based amphoteric clay on TC adsorption by bank soils was explored under different environmental conditions, such as temperature, pH value, and ionic strength, to provide a reference for the study of prevention and repair of TC pollution in breeding areas.

2. Materials and methods

2.1. Experimental materials

Dodecyl dimethyl betaine (BS-12), which was provided by Xingguang Auxiliary Factory (Tianjin City, China), was used as the amphoteric modifier.

TC, the test pollutant, was purchased from Sigma (USA) and had a purity of 99.9%. Three ionizable groups exist in the molecular structure of TC, and the ionization equilibrium constants pK_{a1} , pK_{a2} , and pK_{a3} are 3.30, 7.69, and 9.69, respectively. TC with pH < 3.3 is positively charged, that with pH between 3.3 and 7.7 is positively or negatively charged, and that with pH > 9 exists as an anion [20].

Sodium-based B was purchased from Tongchuang Bentonite Company, Xinyang, Henan and purified by the water-washing method [21]. The basic physicochemical properties of the B after purification were as follows: cation exchange capacity (CEC), 1,000.33 mmol/kg; pH, 9.59; total organic carbon (TOC), 4.98 g/kg.

C was prepared by using *Alternanthera Philoxeroides*. Xerophytes (XAp) and hydrophytes (HAp) were collected from the dry and paddy fields along Fu River. Then, the collected *A. philoxeroides* were washed with deionized water, dried in a 105°C blast-drying oven to constant weight, crushed, and placed in a muffle furnace under the protection of nitrogen for pyrolysis (400°C for 2 h). After reaching the pyrolysis time, the XAp C (XAp-C) and HAp C (HAp-C) could be obtained by passing through a 60 mesh sieve.

BS-12 modified B (BS-B) was prepared by the wet method [22]. In this process, a certain weight of purified B was slowly added to the BS-12 solution prepared previously (mass ratio of solution and B was 10:1; BS-12 was calculated in accordance with the CEC of B). After stirring for 6 h at 40°C in a water bath, BS-B was centrifuged at 4,800 rpm for 10 min. Then, the supernatant was discarded and washed thrice with deionized water by centrifugation. BS-B was obtained after drying at 60°C and then passed through a 60-mesh sieve.

C-based composite materials were prepared by the following method. A total of 10 g B (or BS-B) was placed in a 1 L glass container (0.5 L deionized water) by ultrasonic dispersion and shaken at a constant temperature for 6 h at 150 rpm. Then, 100 g C (XAp-C or HAp-C) was added, and the mixture was continually shaken at a constant temperature for 12 h. Then, the supernatant was obtained after centrifuging, and the lower product was dried at 60°C and passed through a 60-mesh sieve. The four different C-based composite materials that could be obtained were XAp-C/B (XAp-C loaded with B, the same with the rest of the materials), XAp-C/BS-B, HAp-C/B, and HAp-C/BS-B. Table 1 shows the basic physicochemical properties of the composite materials. Fig. 1 shows the scanning electron microscopy (SEM) images of XAp-C/B and XAp-C/BS-B.

The riverbank soils were obtained from MY, SN, and HC in the Sichuan–Chongqing section of Fu River within

Table 1
Basic physicochemical properties of different composite materials

Composite materials	pH values	CEC (mmol/kg)	Specific surface-areas (m ² /g)
XAp-C/B	9.51	332.17	16.34
XAp-C/BS-B	8.37	141.55	7.18
HAp-C/B	9.10	219.39	7.17
HAp-C/BS-B	7.84	116.68	4.51

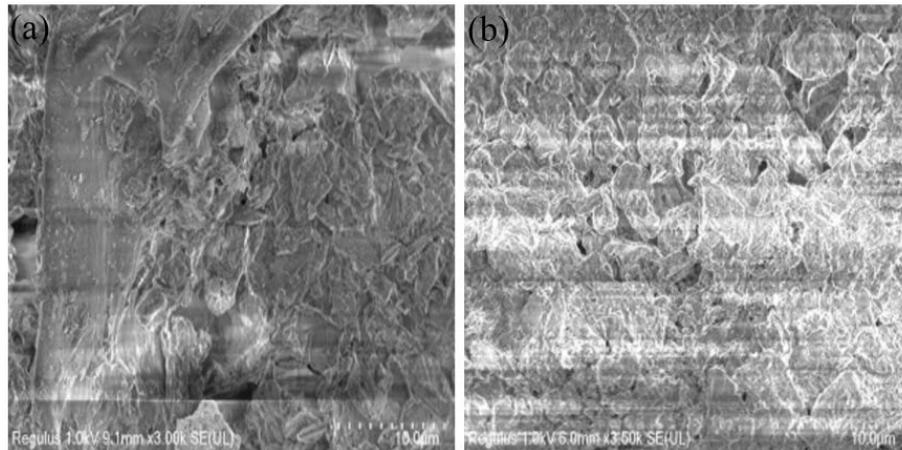


Fig. 1. SEM images of C loaded with B (a) and BS-B (b).

50 m of the riverbank. The surface layer (S, 0–20 cm) and subsurface layer (D, 20–40 cm) soil samples were collected by S-spot method in typical area, mixed evenly, dried and ground, and passed through 100-mesh (0.15 mm) nylon sieve for storage. Table 2 lists the physical and chemical properties of the different soil samples.

2.2. Experimental design

2.2.1. Preparation of amended soil samples

Four types of C-based composite materials with a mass ratio of 1% were added to the S and D layer soil samples of MY, SN, and HC in Fu River, and the mixtures were mixed uniformly to form 24 amended soil samples of $MYS_{XAP-C/B}$ (99% S layer soil of MY + 1% XAP-C/B; the same formula applies to the remaining sample), $MYD_{XAP-C/B}$, $MYS_{XAP-C/BS-B}$, $MYD_{XAP-C/BS-B}$ etc. TC isotherm adsorption experiments were carried out and each treatment was repeated thrice.

2.2.2. Influence of environmental factors

The pH of the initial solution was set to 3, 4, 5, and 6.

The ionic strength of the initial solution was set to 0.01, 0.05, 0.1, and 0.5 mol/L (at which the pH was best controlled).

The experimental temperatures were set to 10°C, 20°C, 30°C, and 40°C (at which the best pH and ionic strength were controlled).

2.2.3. Isothermal adsorption experiment of TC

The initial concentration gradient of TC was set to 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 mg/L. Each treatment was repeated thrice under the best environmental factors.

2.3. Experimental methods

Batch equilibrium method was used for TC adsorption. A total of 0.5000 g samples were weighed in nine 50 mL plastic centrifuge tubes, and 20.00 mL TC solution with different concentration gradients were added to the pipette under optimal environmental conditions with 150 rpm and 12 h oscillation. The equilibrium adsorption of TC in the supernatant was determined by centrifugation at 4,800 rpm for 20 min, the equilibrium adsorption amount of TC was determined, and the equilibrium adsorption amount of each material was calculated by subtraction.

2.4. Data processing

2.4.1. Fitting of adsorption isotherms

Based on the adsorption isotherm trend, Langmuir isotherm was selected to fit the TC adsorption isotherm. Eq. (1) is defined as follows:

$$q = \frac{q_m bc}{1 + bc} \quad (1)$$

Table 2
Basic physicochemical properties of different bank soils

Tested bank soils		pH values	CEC (mmol/kg)	TOC (g/kg)	Specific surface-areas (m ² /g)
S layer	MY	7.80	122.53	25.01	98.25
	SN	7.44	182.79	8.84	103.14
	HC	6.56	100.69	25.83	89.34
D layer	MY	7.68	174.75	15.49	113.25
	SN	7.52	161.46	5.85	122.41
	HC	6.64	116.54	25.28	83.63

where q is the equilibrium adsorption amount of TC for the amended soil, mmol/kg; c is the equilibrium concentration of TC in the solution, mmol/kg; q_m is the maximum adsorption amount of TC for the amended soil, mmol/kg; b is the apparent equilibrium constant of TC adsorption on the amended soil which can be used to measure the affinity of adsorption.

2.4.2. Calculation of thermodynamic parameters

Parameter b in the Langmuir model is equivalent to the apparent adsorption constant of equilibrium constant, and the thermodynamic parameter calculated by $b = K$ or K_a is called the apparent thermodynamic parameter; Eqs. (2)–(4) are as follows:

$$\Delta G = -RT \ln K \tag{2}$$

$$\Delta H = R \left(\frac{T_1 \cdot T_2}{T_2 - T_1} \right) \cdot \ln \left(\frac{K_a' T_2}{K_a' T_1} \right) \tag{3}$$

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

where ΔG is the standard free energy change (kJ/mol), R is a 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

of adsorption process (kJ/mol), and ΔS is the entropy change of adsorption process (J/mol/K).

CurveExpert 1.4 fitting software was used in isothermal fitting, and SigmaPlot 10.0 software was adopted to improve data plotting.

3. Results and discussion

3.1. Effect of pH on TC adsorption by amended soils

Fig. 2 shows the difference in TC adsorption on the test soil samples in the pH range of 3–6. With the increased pH, the adsorption amount of TC on each test sample decreased. The decrease in amplitude of TC adsorption by different amended soils in MY, SN, and HC reached 9.06%–20.22%, 7.66%–17.35%, and 9.12%–17.28%, respectively. The decrease in amplitude of Ap-C/B-amended soil (10.13%–20.22%) was larger than that of Ap-C/BS-B-amended soil (7.66%–16.28%). In addition, the decrease in amplitude of bank soil amended by XAp-C-based materials (9.05%–20.22%) was larger than that amended by HAp-C-based materials (7.66%–18.33%). This finding was attributed in the changes in TC form in the solution with the increase in pH. At pH 3, TC almost existed in cationic form. At this point, the cationic group of TC could bond with the negative charge on the soil surface by ion exchange reaction. With the increase in pH, the proportion of negative charges in TC increased, and the adsorption effect of TC by soil gradually worsened. In addition, as the pH value gradually increased, organic functional

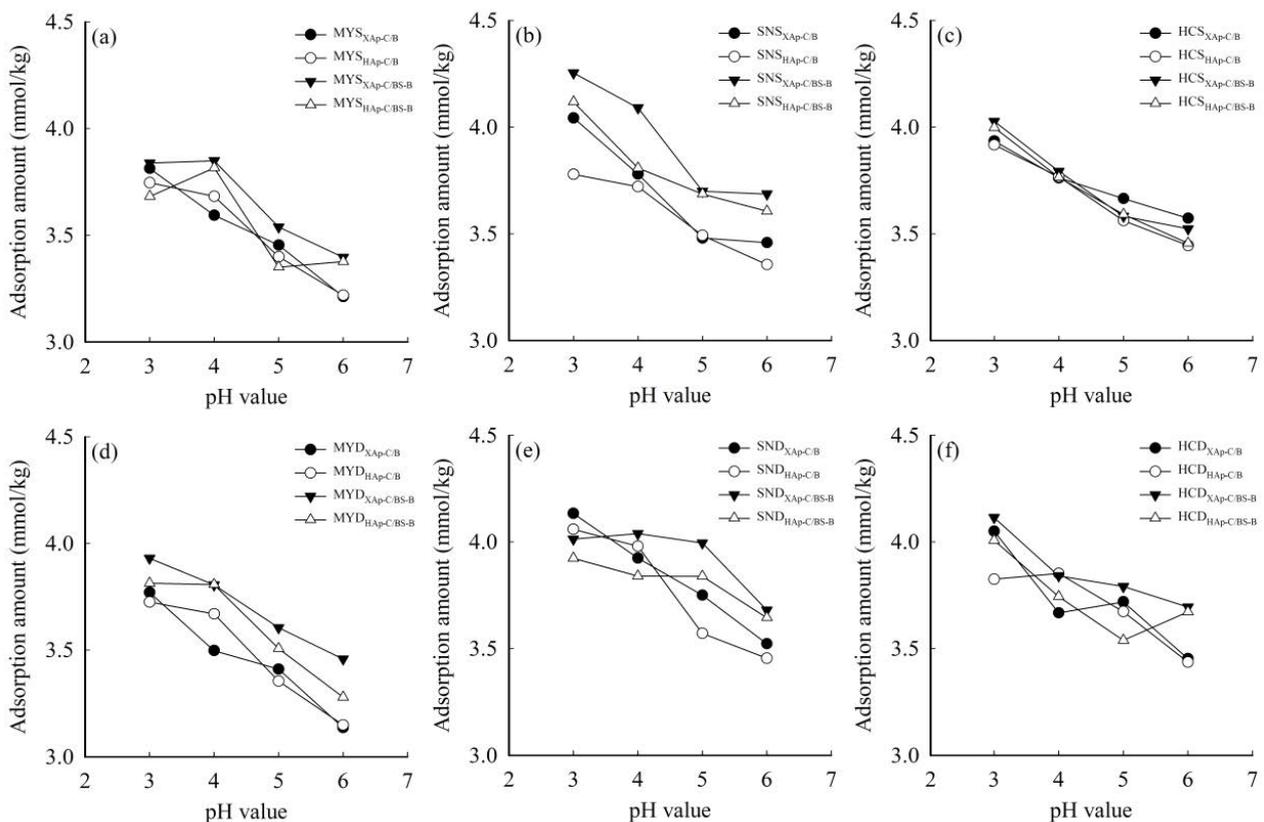


Fig. 2. (a–f) Adsorption amount of TC on the samples at different pH.

groups dissociated, and the negative charge on the clay surface increased, which caused the decrease in TC amount adsorbed by the soils [23].

3.2. Effect of ionic strength on TC adsorption

At the optimal pH (pH = 3), the adsorption amount of TC by each test soil decreased with the increase in ionic strength (I) at the range of 0.01–0.5 mol/L (Table 3). When $I = 0.01$ – 0.05 mol/L, the adsorption amount of TC on the most of test soils slightly decreased, and the decrease ranged from 0.05% to 12.88%. At I between 0.05 and 0.5 mol/L, the decrease significantly enlarged, ranging from 16.81% to 36.53%. Except for $\text{SND}_{\text{XAp-C/B}'} \text{HCS}_{\text{HAp-C/BS-B}'}$ and $\text{HCD}_{\text{XAp-C/B}'}$ the TC adsorption amount of the other soil samples were significantly different under various I treatments. From 0.01 to 0.5 mol/L, the decrease in amplitude of TC adsorption by different amended soils from MY, SN, and HC were ranked in the order of SN (26.62%–44.98%) > MY (27.41%–40.96%) > HC (17.18%–35.49%). The decrease in amplitude of bank soil amended by XAp-C-based materials was consistent with that of the bank soil amended by HAp-C-based materials. The main reason is that as the I increased, the concentration of electrolyte cation increased, forming ion exchange competitive

adsorption with TC, which led to the decreased adsorption amount of TC [24].

3.3. Effect of temperature on TC adsorption on soil samples

At pH = 3 and $I = 0.01$ mol/L, the adsorption amount of TC in each test soil sample increased with the increase in temperature (Fig. 3), showing a positive temperature effect. When the temperature increased from 10°C to 40°C, the increase range of amended MY, SN, and HC soils were 15.73%–24.24%, 4.95%–17.23%, and 11.84%–17.18%, respectively. The increased amplitude of the S layer soil (11.65%–24.24%) was higher than that of the D layer soil (4.95%–20.99%). Although the adsorption performance of MY soil was weaker than that of SN and HC soils, the increase in amplitude of MY soil was the largest. The above results are mainly attributed to the following. With the increase in temperature, the diffusion velocity of TC molecules in the solution increased, the contact rate between TC and the surface of the sample was accelerated, and the endothermic reaction between TC and the sample surface increased. On the other hand, with the increase in temperature, the pores in C became larger, leading to the decreased resistance for TC to enter the pores; the increase in temperature also promoted the ion exchange and hydrophobic interaction between TC and C [25].

Table 3
Adsorption amount of TC on the samples at different ionic strengths

Soil samples	Adsorption amount of TC (mmol/kg)			
	$I = 0.01$ mol/L	$I = 0.05$ mol/L	$I = 0.1$ mol/L	$I = 0.5$ mol/L
$\text{MYS}_{\text{XAp-C/B}}$	3.37a ± 0.21	3.39a ± 0.23	2.69b ± 0.14	2.60b ± 0.15
$\text{MYS}_{\text{HAp-C/B}}$	3.43a ± 0.23	3.23ab ± 0.18	2.68bc ± 0.20	2.57c ± 0.14
$\text{MYS}_{\text{XAp-C/BS-B}}$	3.72a ± 0.28	3.65a ± 0.25	2.77b ± 0.17	2.84b ± 0.18
$\text{MYS}_{\text{HAp-C/BS-B}}$	3.54a ± 0.23	3.54a ± 0.20	2.72b ± 0.18	2.69b ± 0.13
$\text{SNS}_{\text{XAp-C/B}}$	3.85a ± 0.29	3.72ab ± 0.27	2.99bc ± 0.22	2.78c ± 0.20
$\text{SNS}_{\text{HAp-C/B}}$	3.78a ± 0.28	3.50ab ± 0.22	2.87b ± 0.23	2.78b ± 0.22
$\text{SNS}_{\text{XAp-C/BS-B}}$	4.22a ± 0.29	3.80ab ± 0.25	3.23b ± 0.20	3.01b ± 0.19
$\text{SNS}_{\text{HAp-C/BS-B}}$	4.21a ± 0.35	3.74ab ± 0.25	3.19b ± 0.21	2.90b ± 0.21
$\text{HCS}_{\text{XAp-C/B}}$	3.71a ± 0.25	3.69a ± 0.27	2.98a ± 0.20	3.00a ± 0.21
$\text{HCS}_{\text{HAp-C/B}}$	3.81a ± 0.26	3.57ab ± 0.24	2.92b ± 0.21	2.93b ± 0.24
$\text{HCS}_{\text{XAp-C/BS-B}}$	3.71ab ± 0.25	3.95a ± 0.25	3.24ab ± 0.22	3.09b ± 0.21
$\text{HCS}_{\text{HAp-C/BS-B}}$	3.68a ± 0.27	3.67a ± 0.23	3.02a ± 0.21	3.14a ± 0.20
$\text{MYD}_{\text{XAp-C/B}}$	3.76a ± 0.26	3.42ab ± 0.21	2.81b ± 0.21	2.67b ± 0.20
$\text{MYD}_{\text{HAp-C/B}}$	3.68a ± 0.29	3.26ab ± 0.28	2.80b ± 0.19	2.78b ± 0.21
$\text{MYD}_{\text{XAp-C/BS-B}}$	3.62a ± 0.22	3.61a ± 0.23	3.08ab ± 0.17	2.84b ± 0.17
$\text{MYD}_{\text{HAp-C/BS-B}}$	3.67a ± 0.27	3.40ab ± 0.21	2.89ab ± 0.23	2.78b ± 0.20
$\text{SND}_{\text{XAp-C/B}}$	4.00a ± 0.30	3.91ab ± 0.14	3.13b ± 0.25	3.01b ± 0.21
$\text{SND}_{\text{HAp-C/B}}$	3.89a ± 0.29	3.60a ± 0.22	3.32a ± 0.27	3.07a ± 0.19
$\text{SND}_{\text{XAp-C/BS-B}}$	4.19a ± 0.31	4.03a ± 0.27	3.16b ± 0.21	3.18b ± 0.20
$\text{SND}_{\text{HAp-C/BS-B}}$	4.10a ± 0.26	3.69ab ± 0.29	3.12b ± 0.20	3.07b ± 0.23
$\text{HCD}_{\text{XAp-C/B}}$	3.98a ± 0.27	4.01a ± 0.25	3.23ab ± 0.22	2.94b ± 0.19
$\text{HCD}_{\text{HAp-C/B}}$	3.77a ± 0.26	3.76a ± 0.23	2.97b ± 0.22	2.94b ± 0.20
$\text{HCD}_{\text{XAp-C/BS-B}}$	3.94a ± 0.27	3.88a ± 0.29	3.15a ± 0.23	3.08a ± 0.23
$\text{HCD}_{\text{HAp-C/BS-B}}$	3.83a ± 0.26	3.77a ± 0.24	3.00b ± 0.24	2.88b ± 0.20

Different lowercase letters indicate significant difference among treatments at 0.05 levels.

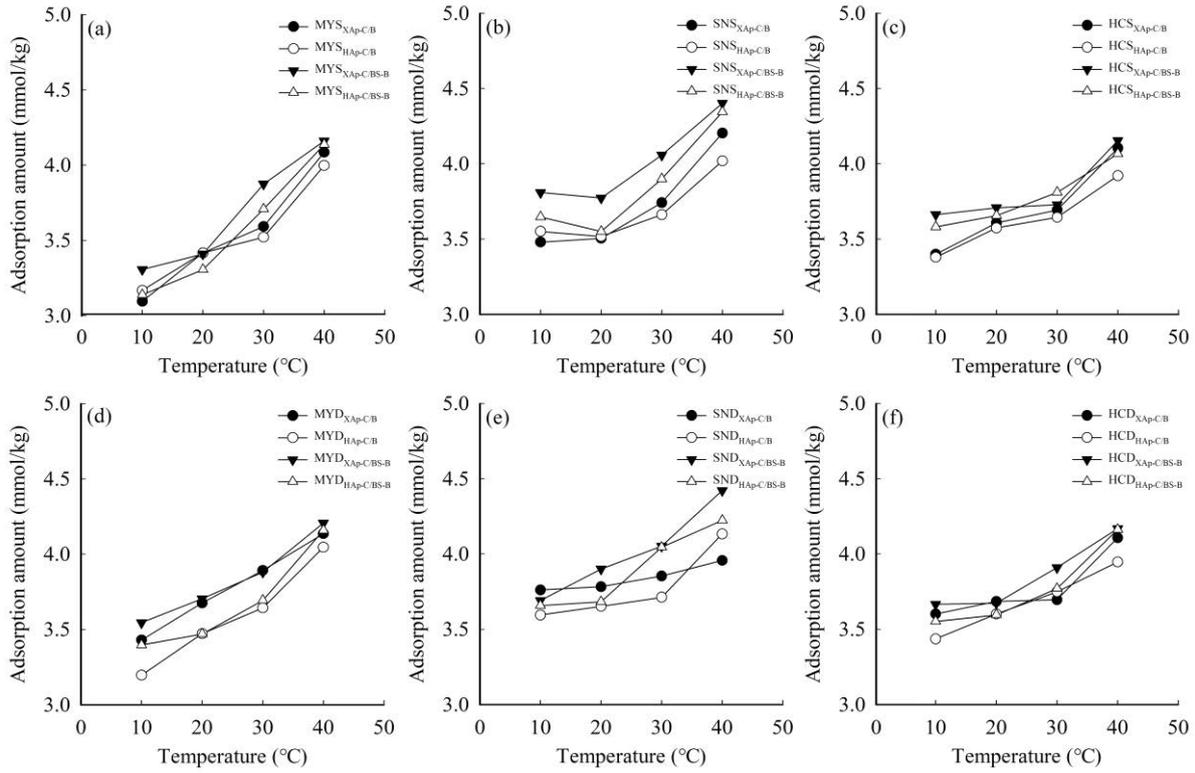


Fig. 3. (a–f) Adsorption amount of TC on the samples at different temperatures.

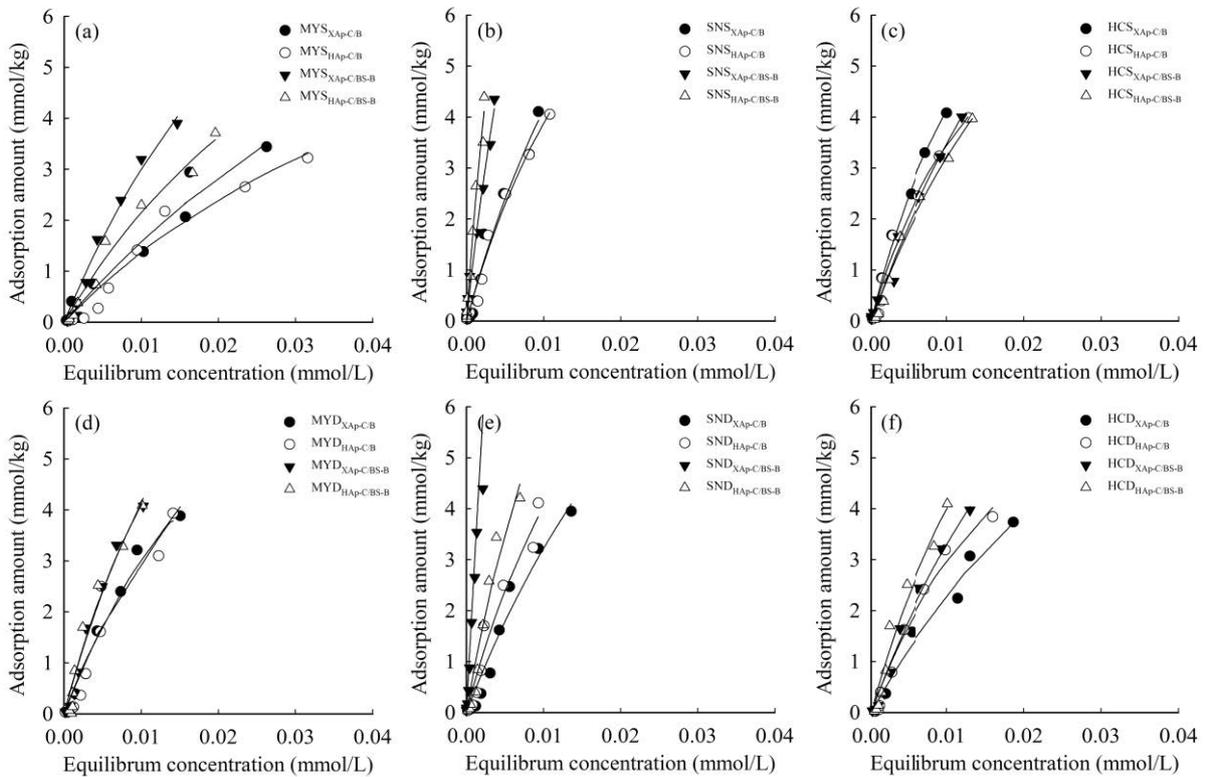


Fig. 4. (a–f) Adsorption isotherms of TC on the different soil samples.

3.4. TC adsorption isotherms for different test samples

Fig. 4 shows the adsorption isotherm of TC on different amended soils under the most suitable environmental conditions (pH = 3, $I = 0.01$ mol/L, and 40°C). The adsorption isotherms of TC on different soil samples were all “L” type. Langmuir adsorption isotherm equation was used to fit the isothermal data of TC adsorption, and the fitting parameters are shown in Table 4. The fitting coefficients were all greater than 0.96 and showed a very significant correlation, indicating that the Langmuir model could describe well the process of TC adsorption. Table 3 shows that the maximum adsorption amount (q_m) of TC for each amended soil was in the range of 9.33–21.29 mmol/kg, and q_m was ranked in the order of SN > HC > MY under the same soil improving conditions. Under the same soil sample, the q_m of bank soil amended by XAp-C-based materials was larger than that by HAp-C-based materials. The q_m of Ap-C/BS-B-amended soil was larger than that of Ap-C/B-amended soil. The affinity constant b of each amended soil for TC adsorption was maintained in the range of 12.40–148.64, implying a strong adsorption affinity. The average adsorption rate of TC was kept above 65%, and the highest value was 98.47%. The average adsorption rate of Ap-C/BS-B-amended soil was higher than that of Ap-C/B-amended soil.

C has a high specific surface area and abundant surface adsorption sites. Adding C can increase the adsorption capacity of TC in soil by about 1.2 times, and the q_m can reach up to 19.9 mmol/kg with 1% adding proportion [26]. Compared with the above result, the C-based composite material used in soil improvement has a higher adsorption capacity for TC and is thus a good soil improvement material.

3.5. Correlation between q_m and physicochemical properties of bank soil

Fig. 5 shows the linear fitting results between q_m and the physicochemical properties of bank soil. The correlation of CEC and q_m was moderate and had a significant correlation with q_m of HAp-C/B-amended soils. TOC was negatively correlated with q_m and showed a significant correlation with q_m of XAp-C/B, XAp-C/BS-B, and HAp-C/BS-B-amended soils. A poor correlation was observed between pH and q_m , S_{BET} and q_m . The above results showed that soil CEC and TOC played a key role in determining the adsorption effect of TC on different amended soils. CEC on the soil surface can provide the number of adsorption points for TC; the high number of adsorption points results in strong ion exchange [1]. The TOC in the soil sample occupied

Table 4
Langmuir fitting parameters of TC adsorption by each amended soil

Soil samples	Correlation coefficients/ r	q_m (mmol/kg)	b (L/mmol)	Average adsorption rate (%)	ΔG (kJ/mol)		ΔH (kJ/mol)	ΔS [J/(mol·K)]
					10°C	40°C		
MYS _{XAp-C/B}	0.9790**	14.35	12.40	76.42	-5.68	-7.01	10.07	60.35
MYS _{HAp-C/B}	0.9785**	9.55	16.79	65.32	-6.60	-7.85	7.60	54.58
MYS _{XAp-C/BS-B}	0.9915**	15.43	24.18	81.46	-7.11	-8.46	8.14	58.61
MYS _{HAp-C/BS-B}	0.9885**	11.60	22.76	77.54	-6.96	-8.37	9.23	62.17
SNS _{XAp-C/B}	0.9821**	15.35	37.13	88.98	-8.12	-9.47	6.75	57.29
SNS _{HAp-C/B}	0.9913**	12.76	43.47	92.07	-8.57	-9.80	4.42	50.21
SNS _{XAp-C/BS-B}	0.9937**	21.29	67.45	98.00	-9.60	-10.99	5.16	57.05
SNS _{HAp-C/BS-B}	0.9897**	18.98	120.65	98.47	-10.85	-12.45	6.25	66.04
HCS _{XAp-C/B}	0.9921**	13.87	42.44	89.26	-8.40	-9.76	6.56	57.65
HCS _{HAp-C/B}	0.9897**	9.33	58.72	88.04	-9.20	-10.61	5.99	58.64
HCS _{XAp-C/BS-B}	0.9927**	18.40	23.25	92.62	-7.20	-8.29	4.56	45.40
HCS _{HAp-C/BS-B}	0.9923**	14.12	29.41	83.60	-7.72	-8.91	5.16	49.69
MYD _{XAp-C/B}	0.9884**	12.99	30.22	81.49	-7.73	-9.02	6.44	54.58
MYD _{HAp-C/B}	0.9683**	10.66	38.72	85.17	-8.12	-9.53	7.53	60.24
MYD _{XAp-C/BS-B}	0.9883**	15.32	37.21	88.24	-8.19	-9.47	5.78	53.88
MYD _{HAp-C/BS-B}	0.9743**	13.43	43.99	79.66	-8.47	-9.90	7.25	60.57
SND _{XAp-C/B}	0.9802**	16.75	23.95	85.02	-7.36	-8.28	1.81	35.62
SND _{HAp-C/B}	0.9783**	13.00	44.86	88.91	-8.64	-9.92	4.98	52.62
SND _{XAp-C/BS-B}	0.9909**	18.93	148.64	98.23	-11.36	-13.04	6.44	68.79
SND _{HAp-C/BS-B}	0.9686**	16.77	52.46	91.06	-8.99	-10.32	5.13	54.58
HCD _{XAp-C/B}	0.9901**	13.64	20.24	78.10	-6.99	-8.09	4.93	46.00
HCD _{HAp-C/B}	0.9881**	10.08	41.44	81.06	-8.51	-9.83	5.83	55.30
HCD _{XAp-C/BS-B}	0.9970**	16.15	25.87	86.15	-7.47	-8.62	4.91	47.78
HCD _{HAp-C/BS-B}	0.9790**	13.90	40.13	84.58	-8.39	-9.65	5.09	52.08

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

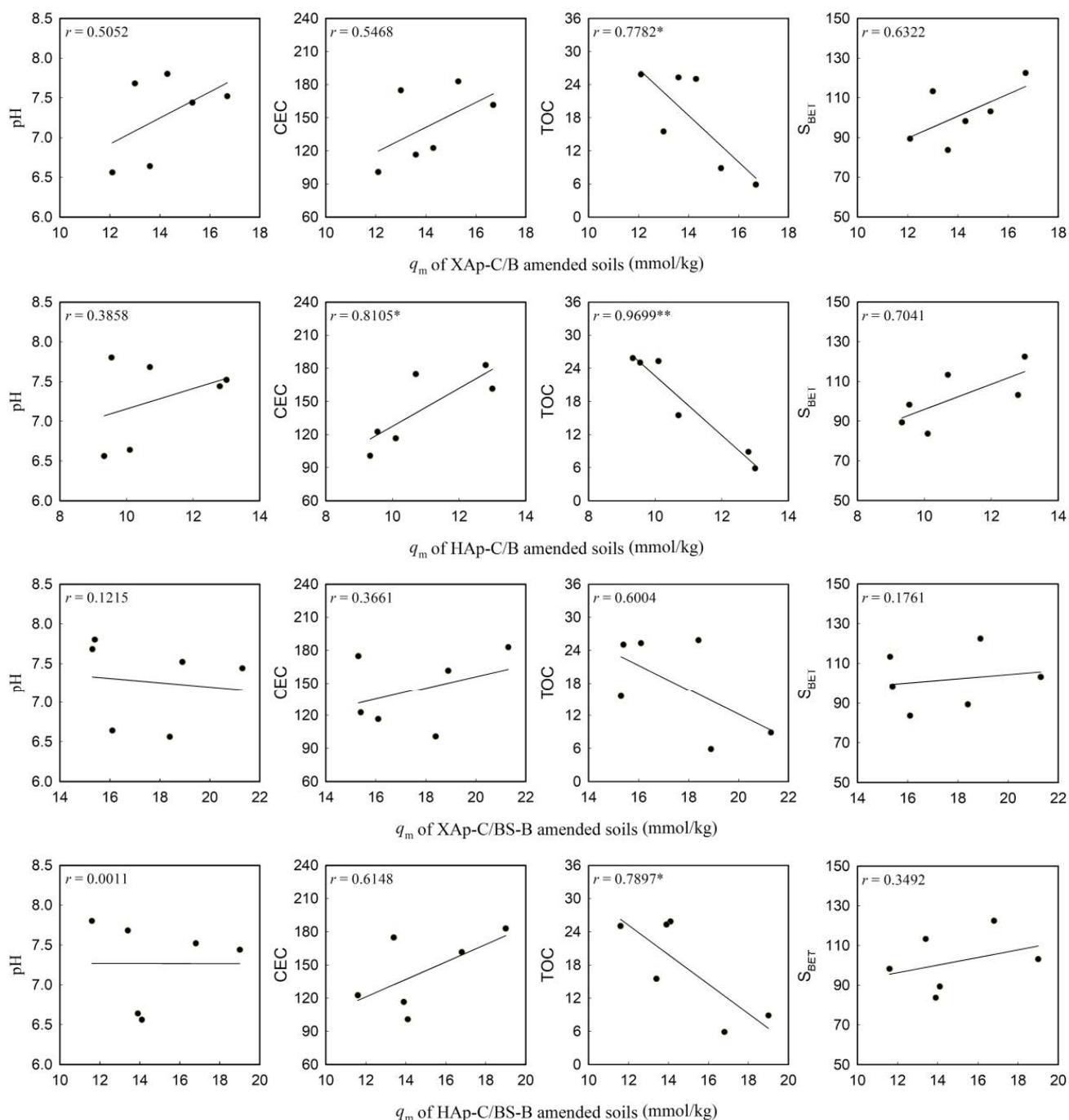


Fig. 5. Analytical parameters of physicochemical properties and q_m . * and ** indicate a significant correlation at the level of $p = 0.05$ or 0.01 . When $f = 5$, and $p = 0.05$ or 0.01 , $r = 0.754$ or 0.874 .

the adsorption site on the soil sample, thus inhibiting the TC adsorption capacity of the soil sample. Thus, the q_m of TC was negatively correlated with the TOC content.

4. Conclusion

- As the pH increased from 3 to 6, the adsorption amount of TC to each amended riverbank soil decreased.

In the range of 10°C–40°C, TC adsorption amount of the test material increased with the increase in temperature. The adsorption amount of TC in the soil samples decreased with the ionic strength in 0.01–0.5 mol/L.

- The adsorption isotherm of TC on different amended soils were all accorded with Langmuir model. The q_m of TC for each amended soil was in the range of

9.33–21.29 mmol/kg, and q_m was ranked in the order of SN > HC > MY under the same soil-improving conditions.

- The TC adsorption of each amended soil was a spontaneous, endothermic, and entropy-adding process. The CEC and TOC of soil samples are the keys to determining the adsorption effect of TC.

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