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Effects of Pig Manure Biochar on Adsorption of Tetracycline from Saline Soil at Different Depths

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Abstract:

The static adsorption experiment was used to study the adsorption performance of tetracycline (TC) on saline soil with different depths in cotton fields in southern Xinjiang. The effects of pig shit biochar (PSBC) prepared at 600℃ on the adsorption of saline soil were studied. The kinetic and thermodynamic adsorption processes were analyzed, and the effects of temperature, pH and ionic strength on the adsorption were clarified. FTIR and XRD were carried out on the saline soil system before and after adsorption in order to reveal the adsorption mechanism of TC on saline soil, which provide a certain basis for ecological risk assessment of TC. The results showed that the adsorption process of TC on the saline soil of cotton field accorded with the quasi-second-order kinetic model, and the adsorption process consisted of fast adsorption process and slow adsorption process, and the adsorption reached equilibrium within 6 hours; TC adsorption capacity decreased with the increase of soil depth, and the surface soil with high organic matter content and clay content had stronger adsorption capacity, but the addition of biochar changed the adsorption mechanism of the original saline soil system. Therefore, it results in a significant increase in adsorption capacity of deep soil and higher than that of surface soil. Adsorption isothermal process accords with Linear and Freundlich model, adding biochar can increase adsorption partition coefficient Kd and affinity of saline soil at different depths; When the temperature rises, the adsorption is favorable, and the adsorption capacity is the highest when the pH of the solution system is 7.The adsorption of TC by saline soil involves both physical and chemical processes, including π-π electron donor acceptor interaction, cation exchange, electrostatic interaction and pore filling effect.

Keywords: *Saline soil, Tetracycline, Manure biochar, Sorption behavior, Influential factors.*

Forest Chemicals Revew
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I. INTRODUCTION

Antibiotics, organic metabolites produced by organisms (including microorganisms, plants and animals) during their life activities, are widely used in fields like agricultural production, animal husbandry, human and animal disease prevention. At present, according to chemical structure, the antibiotics detected by the environmental system can be divided into macrolides, β-lactams, tetracyclines, sulfonamides, amino acid glycosides, quinolones, etc. Where, tetracyclines (TCs) is the most used variety, accounting for 45.90%. According to reports, about 70%~90% TCs cannot be effectively metabolized by organisms, which are released into the environment with excrement. Studies have shown that the average mass fraction of tetracycline in agricultural soil in China ranges between 0~2450 μg/kg [1], so it is necessary to seek effective measures to alleviate soil antibiotic pollution.

Biochar is produced by pyrolysis and carbonization of agricultural waste materials under anaerobic or anoxic conditions, which has strong adsorption and can improve the physical and chemical properties of soil. The preparation of organic solid waste from livestock and poultry into biochar with higher added value can effectively solve the problems of low utilization rate of agricultural waste resources and serious pollution [2]. The addition of biochar is an effective way to improve the physical and chemical properties of saline soil. Regarding its effect, significant effects are shown in terms of changes in soil physical and chemical properties, enhancement of soil fertility, and improvement of agronomic performance. Research on its related mechanisms has recently become an opportunity and challenge for the improvement research of saline soil [3]. Addition of biomass charcoal will lower the migration performance and bioavailability of pollutants in the soil. The effect of adsorption cannot be ignored. It directly affects the leaching rate and depth of veterinary drug antibiotics in soil [4]. Hence, clarifying the impact of adsorption on persistence and effectiveness of antibiotics in the soil environment is an important indicator for the safety assessment of antibiotic use. Studies have shown that tetracycline antibiotics have strong adsorption capacity and weak migration capacity in the soil environment. Factors affecting its adsorption performance include the type of organic matter, soil mechanical composition, the nature of tetracycline itself, and the interaction between microbial activities.

Currently, 75 countries worldwide are affected by soil salinity. The area of saline-alkali land is about 9.50×10^7 hm^2. In addition, 7.70×10^7 hm^2 of soil is in a state of secondary salinization, which limits crop production around the world. It is estimated that by 2050, more than 50% cultivated land will be affected by salinization. In China, the usable saline-alkali land area is about 3.67×10^7 hm^2, of which about 0.67×10^7 hm^2 saline-alkali land has the potential for agricultural improvement and utilization [5]. Soil salinization may induce serious soil

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hardening, increased nutrient leaching, reduced fertilizer efficiency, and reduced crop yields [6], which has become a hindering factor in the sustainable development of agricultural economy in southern Xinjiang. The previous finding by the research team reveals that biochar can be used as a saline-alkali land improvement substance to improve the physical and chemical properties of the saline soil, increase the nutrient content and effectiveness of saline soil, and improve the water and salt transport in the saline soil. However, the application of animal manure-based biochar may bring about soil environment pollution due to veterinary antibiotics, and the migration behavior of tetracycline antibiotics in the saline soil environment and the effect of biochar addition on the migration of tetracycline lack research foundation support. In addition, as far as the current research is concerned, more in-depth analysis and research is conducted on the adsorption mechanism of soil against organic pollutants, but there is less research on the longitudinal adsorption and migration of organic pollutants in saline soil and its influencing factors. Therefore, this paper uses tetracycline as the target pollutant to study the effect of pig manure biochar addition on the adsorption of tetracycline in saline soil at different depths and its mechanism of action. The effects of temperature, pH and ionic strength on the adsorption characteristics are investigated, and the adsorption mechanism of tetracycline in saline soil is clarified to provide a theoretical basis for the control and treatment of tetracycline in saline soil.

II. MATERIALS AND METHODS

2.1 Soils

The saline soil samples were collected from the cotton planting area in Alar City. The soil samples were collected at a depth of 0-20, 20-40 and 40-60 cm, with weeds, stones and other debris removed. The samples were kept away from light and dried naturally, and screened through a 60-mesh sieve for later use. No biochar was applied to the soil samples, and no antibiotics were detected. The basic physical and chemical properties are shown in Figure 1:

Forest Chemicals Revew
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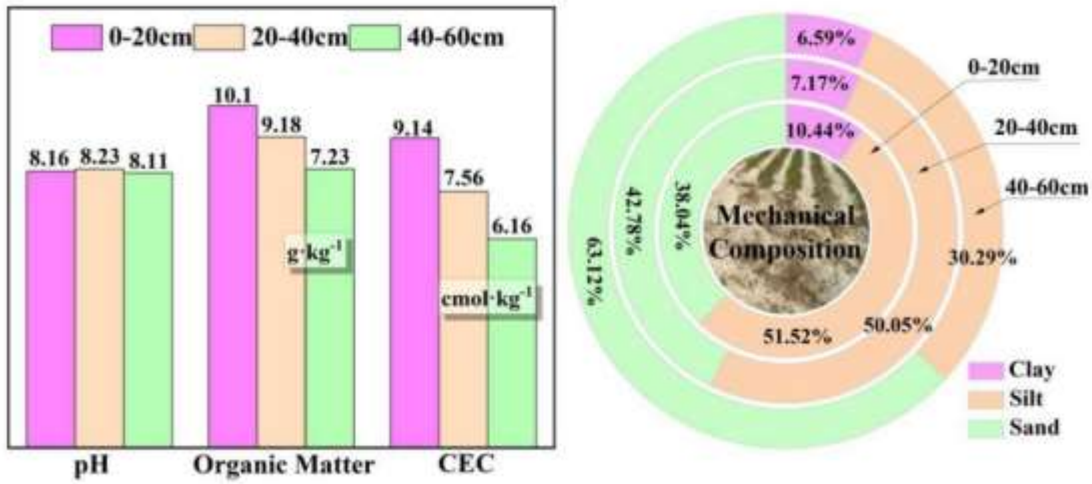

Fig 1: Physical and chemical properties of saline soil at different depths

2.2 Preparation and Characterization of Biochar

Biochar was prepared with pig manure (PS) from the farm as the precursor material, and the pig manure was dried, crushed, and then placed in a brown bottle for later use. Weigh a certain amount of pig manure biomass powder, place it in a tubular muffle furnace, crack at 600°C for 4 h, cool down naturally, grind and screen it through a 60-mesh sieve for later use. The pig manure biochar sample is marked as PSBC.

The elemental analyzer (Elementar micro cube; Elementar Trading(Shanghai) Co., Ltd) was used to measure the composition of C, H, N elements in the biochar, and the specific surface area analyzer (BET; Mike ASAP2460, American Mike Instrument Company) was used to determine the specific surface area, pore volume and pore diameter of biochar (as shown in Table I); Fourier infrared spectroscopy (FTIR); (Perkin Elmer spectrum 100; Perkin Elmer, USA); X-ray diffractometer (XRD) (BRUKER D8 ADVANCE; Bruker, Germany) was used to analyze biochar mineral composition. FTIR and XRD analysis were performed on the samples to investigate the adsorption mechanism before and after adsorption.

TABLE I. Physical and chemical properties of biochar

ITEM	TEMPERATURE	C	N	H	O	H/C	O/C	(N+O)/C	ASH	SPECIFIC

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
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										SURFACE AREA
PSBC	600	28.87	1.65	1.862	0.138	0.064	0.005	0.062	67.48	57.397

2.3 Adsorption Experiment

2.3.1 Adsorption kinetics

Sequencing batch equilibrium method was used for adsorption test. Accurately weigh 0.5 000 g saline soil and 0.0 200 g pig manure biochar, place it into a 50.00 mL centrifuge tube, and add 25.00 mL tetracycline solution with a mass concentration of 25.00 $mg \cdot L^{-1}$. The full temperature oscillator with a rotation speed of 180 $r \cdot min^{-1}$ oscillated at 25℃ in dark. The oscillation time was controlled to be 10, 30, 60, 90, 120, 180, 240, 270, 360, 480 min. After sampling, it was centrifuged at 4000 $r \cdot min^{-1}$ for 20 min, the supernatant was filtered through a 0.45 μm filter membrane, and the sample was analyzed using an ultraviolet-visible spectrophotometer.

2.3.2 Adsorption Thermodynamics

Accurately weigh 0.5 000 g saline soil and 0.0 200 g pig manure biochar, place them into a 50.00 mL centrifuge tube, add 10, 20, 30, 40, 60, 80 and 100 $mg \cdot L^{-1}$ tetracycline solution 25.00 mL, shake at full temperature oscillator with a rotation speed of 180 $r \cdot min^{-1}$, oscillate for 8 h in dark at 25℃, centrifuge for 10 min, and test the sample. The above method was used for the isotherm adsorption experiment under 35℃ and 45℃.

2.3.3 Experiment on influencing factors

Follow the method in section 2.3.1.

pH influence: Adjust the pH to 3, 5, 7, 9 and 11 before adsorption with NaOH or HCl dilute solution. Ionic strength experiment: Choose 4 kinds of saline soil ions, Na^+, K^+, Mg^{2+} and Ca^{2+}, as investigation ions, the concentrations were respectively 0.00, 0.01, 0.10, 1.00 $mol \cdot L^{-1}$.

2.4 Data Processing

2.4.1 Calculation of adsorption capacity and removal rate

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
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The calculation method for tetracycline adsorption (q_e) and removal rate (R) is as follows:

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

$$R(\%)=\frac{(C_0\text{-}C_e)}{C_0}\times 100\% \tag{2}$$

Where, q is the equilibrium adsorption capacity, mg·g^{-1}; C_0 is the initial concentration of TC in the solution, mg·L^{-1}; C_e is the concentration of TC in the adsorption equilibrium solution, mg·L^{-1}; V is the solution volume, L; m is the addition amount of biochar, g; R is the removal rate of TC, %.

2.4.2 Adsorption model

The kinetic process of TC adsorption by saline soil is fitted with a quasi-first-order kinetic model, a quasi-second-order kinetic model, and an intra-particle diffusion model [7], and the formulas are as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 \cdot q_e^2} \tag{4}$$

$$q_t = K_d \cdot t^{0.5} + C \tag{5}$$

Where, q_e is the saturated adsorption capacity of saline soil against TC, mg·g^{-1}; q_t is the adsorption capacity of saline soil against TC at time t, mg·g^{-1}; K_1 is the quasi-first order kinetic rate constant, min^{-1}; K_2 is the quasi-second-order kinetic rate constant, g·mg^{-1}·min^{-1}; K_d is the rate constant of the intra-particle diffusion model, g·mg^{-1}·min$^{0.5}$; C reflects the marginal layer effect.

Linear, Langmuir and Freundlich isotherm adsorption equations [8] are used to fit the adsorption of TC by saline soil.

$$q_e = K_{L1} \cdot C_e \tag{6}$$

Forest Chemicals Revew
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$$\frac{C_e}{q_e}=\frac{1}{q_{\max}}\cdot C_e+\frac{1}{K_L\cdot q_{\max}} \tag{7}$$

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \tag{8}$$

Where, K_L and $q_{max}(mg\cdot g^{-1})$ are respectively the constants and maximum adsorption capacity related to adsorption capacity and adsorption strength in the Langmuir model; K_F is Freundlich constant, and the magnitude of 1/n concerns the nonlinearity of adsorption isotherm.

III. RESULTS AND DISCUSSION

3.1 Adsorption Kinetics

The adsorption capacity of saline soil at different depths presents an increasing trend with the extension of time as shown in Figure 2. TC adsorption capacity increases rapidly in the first 0-60 min, with adsorption capacity between 0.83~1.01 mg/g, and its adsorption capacity is 89%-95% of the equilibrium adsorption capacity. TC adsorption capacity tends to increase slowly in 60-180 min interval, the adsorption gradually reaches equilibrium after 360 min, and the adsorption capacity is 0.88~1.06 mg/g at this time. Experimental studies have shown that TC adsorption by saline soil is a rapid adsorption process, which is consistent with the results of soil adsorption of tetracycline found by Fernández-Calviño and Bao [9, 10]. However, Yan et al., [11] also found that TC adsorption by soil maintained equilibrium for more than 24 hours. It can be seen from Figure 2 that the adsorption amount increases rapidly in the early stage. This may be because adsorption mainly occurs on the surface of saline soil particles. Such physical adsorption and distribution are usually completed in a short period of time. With the extension of adsorption time, the surface adsorption sites are occupied by TC, TC will break through the particle water molecule layer to enter the soil micropores, and then diffuse into the internal pore structure of the particles through the matrix [12]. The adsorption rate gradually decreases at this time.

TC adsorption by the saline soil increased significantly after addition of pig manure biochar, and the rapid adsorption still occurred within 180 min, which may be related to the lower organic content of the saline soil. Addition of biochar resulted in the introduction of a large number of adsorption sites, which increased the surface adsorption and void filling capacity, but could not change the physical adsorption process of saline soil. Studies have shown that during the rapid adsorption process, the distribution of organic matter by soil organic matter and the physical adsorption of organic matter by the mineral surface are essential. The

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distribution and adsorption of organic pollutants in the soil mainly involve van der Waals force, hydrogen bond, dipole force and induced dipole force. Usually, such force can be implemented in a short time [13]. The adsorption of saline soil added with pig manure biochar displayed a slight increase after 1200 min, and the adsorption process may reach equilibrium in a longer period of time. The slow adsorption process is mainly controlled by the pore diffusion process. The pig manure biochar has more developed pore structure. Addition of biochar to the saline soil will affect the pore diffusion process of TC, which will prolong the slow adsorption process, thereby enhancing TC adsorption on saline soil.

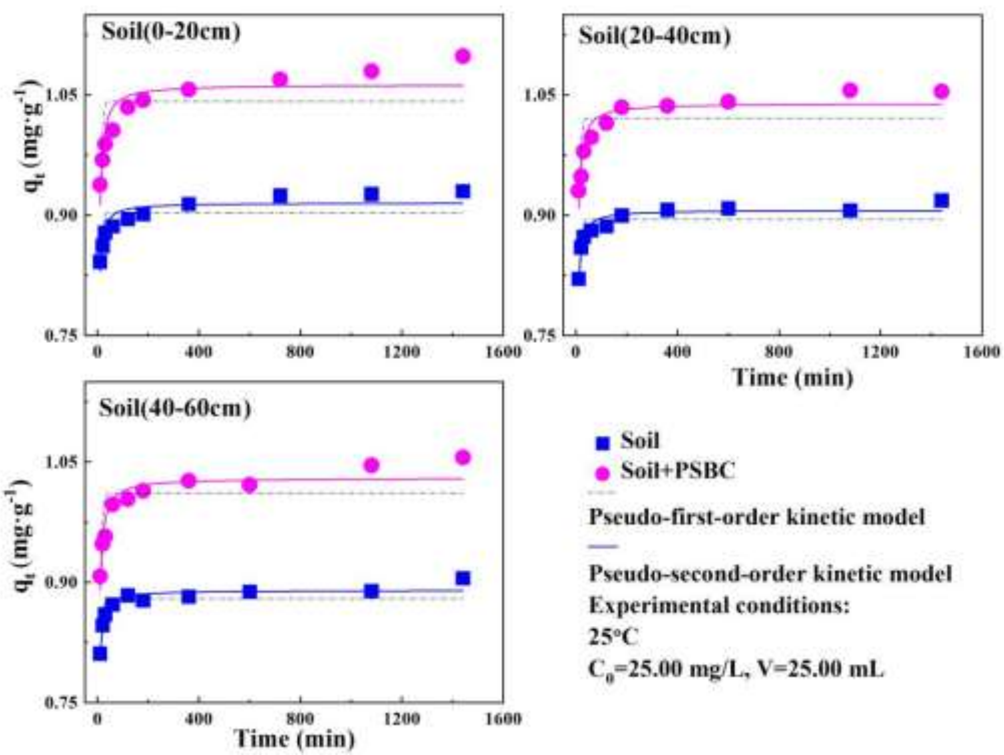

Fig 2: Kinetic curve of TC adsorption by saline soil

The quasi-first-order and quasi-second-order kinetic models were used to fit the experimental data, with the fitting results shown in Table II. Quasi-second-order kinetic model has higher r^2 value than quasi-first-order kinetic model, and the fitting results are fine. The saturated adsorption q_e of the quasi-second-order kinetics fitting approaches the experimentally measured value, indicating that TC adsorption by saline soil added with pig manure biochar and original saline soil more obeys the quasi-second-order kinetic model, and the adsorption rate is mainly controlled by chemical adsorption, including surface adsorption, liquid film diffusion, electron sharing and transfer, and intra-particle diffusion. The number of active sites on the soil surface is positively related to the adsorption capacity of saline soil. The carboxyl

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groups on the surface of TC molecules are easily bonded with mineral ions, and there are weak hydrogen bonds between the surface hydroxyl groups and the hydroxy functional group on the outer surface of the soil [14].

TABLE II. Adsorption kinetics parameters of TC onto saline soil

SAMPLE	PSEUDO-FIRST-ORDER KINETIC MODEL			PSEUDO-SECOND-ORDER KINETIC MODEL		
	K_1/min^{-1}	q_e/mg·g^{-1}	R_1^2	$K_2/g\cdot(mg\cdot min)^{-1}$	q_e/mg·g^{-1}	R_2^2
SOIL(0-20CM)	0.2603	0.9035	0.3976	1.0707	0.9156	0.8312
SOIL(L0-20CM)+PSBC	0.2166	1.0419	0.3758	0.5787	1.6630	0.8116
SOIL(20-40CM)	0.2423	0.8950	0.6278	1.0159	0.9066	0.9382
SOIL(20-40CM)+PSBC	0.2286	1.0211	0.3963	0.6732	1.0396	0.8622
SOIL(40-60CM)	0.2484	0.8798	0.6476	1.0121	0.8903	0.9386
SOIL(40-60CM)+PSBC	0.2160	1.0111	0.4716	0.6261	1.0300	0.8766

In order to further investigate the steps of adsorption rate control, the intra-particle diffusion model was used to fit the saline soil adsorption data. It can be seen from Figure 3 that according to the magnitude of the adsorption rate, the adsorption is carried out in three parts, and the linear fitting results correspond to surface diffusion, intra-particle diffusion and adsorption equilibrium respectively [15]. In the three stages of curve fitting, the straight line does not pass through the origin, indicating that TC adsorption by saline soil is a multi-step process.K_{d1} is high in the first stage, and external diffusion dominates the adsorption process. The diffusion time in this stage is generally shorter, molecular diffusion and membrane diffusion is the main mechanisms [16]. The diffusion rate of saline soil added with pig manure biochar is higher than that of original soil. For its reason, the increase in the external surface area of the pig manure biochar provides more adsorption sites for adsorption. The slope is relatively slow in the second stage, indicating that TC adsorption gradually transits from the liquid film diffusion process to intra-particle diffusion stage. TC transfers across the liquid film to the pores of the biochar and saline soil matrix. At this time, the difference between the adsorbents becomes insignificant. In the third stage of adsorption, after the saline soil fully adsorbs and fills the pores, the intra-particle diffusion rate decreases. Nevertheless, it is possible that due to activation, TC molecules further migrate on the surface slowly until they enter the pores of the particles. The intercept C represents the thickness range of the boundary layer, that is, the larger the intercept, the greater the boundary layer effect [17]. The values of C_2 and C_3 shown in Table III are both greater than C_1, and the diffusion boundary effect is more significant in the latter two stages, indicating that liquid film diffusion and intra-particle diffusion is the main control steps.

Forest Chemicals Revew
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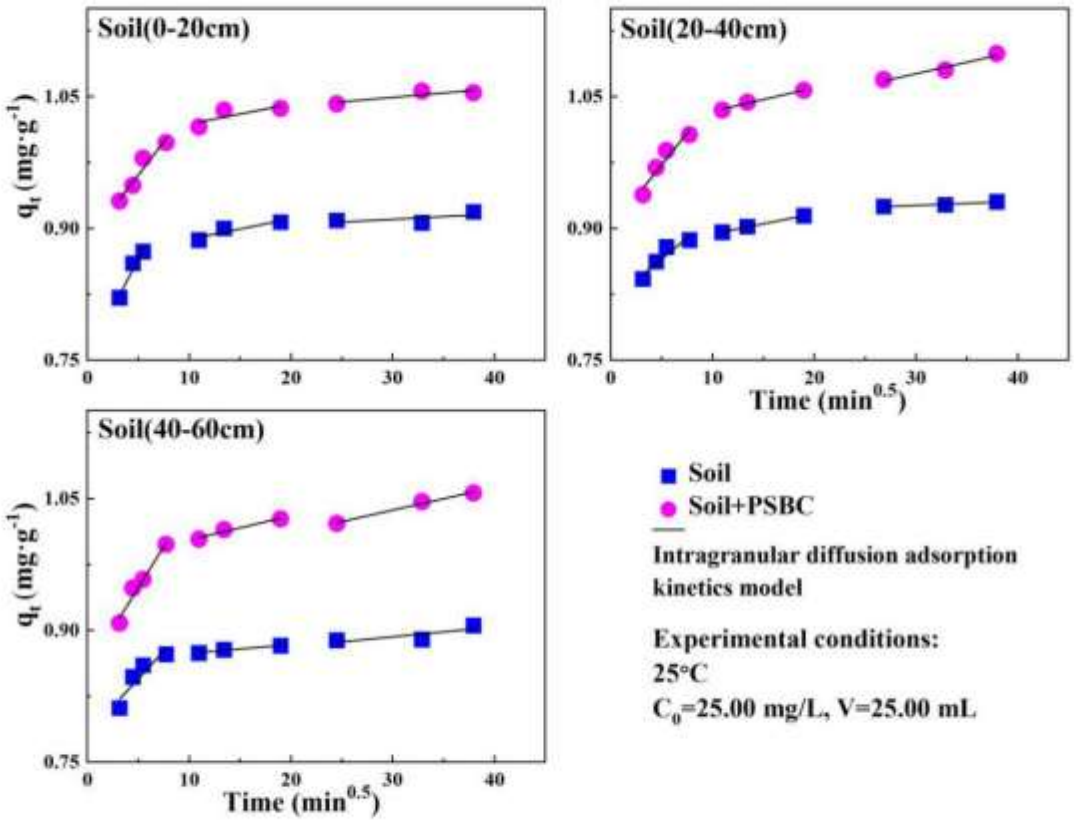

Fig 3: Fitting curve of intra-particle diffusion model regarding TC adsorption by saline soil

TABLEIII. Fitting parameters of intra-particle diffusion model regarding TC adsorption by saline soil

SAMPLE	K_{D1}	C_1	R_1^2	K_{D2}	C_2	R_2^2	K_{D3}	C_3	R_3^2
SOIL(0-20CM)	0.0095	0.8177	0.8851	0.0023	0.8706	0.9992	0.0005	0.9118	0.9470
SOIL(L0-20CM)+PSBC	0.0145	0.8999	0.9224	0.0027	1.0062	0.9896	0.0026	0.9977	0.9591
SOIL(20-40CM)	0.0230	0.7512	0.9603	0.0023	0.8643	0.8533	0.0006	0.8916	0.4137
SOIL(20-40CM)+PSBC	0.0149	0.8864	0.9325	0.0023	0.9962	0.6134	0.0010	1.0187	0.7757
SOIL(40-60CM)	0.0126	0.7821	0.8493	0.0010	0.8636	0.9712	0.0011	0.8583	0.6662
SOIL(40-60CM)+PSBC	0.0187	0.8553	0.9682	0.0028	0.9749	0.9691	0.0026	0.9585	0.9885

K_{di} [mg·(g· min$^{0.5}$)$^{-1}$] is Rate constants of the diffusion model in particles;

C_i (mg·g^{-1}) is a constant related to boundary layer thickness.

3.2 Sorption Isotherm

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
Article History: Received: 12 May 2021 Revised: 25 June 2021 Accepted: 22 July 2021 Publication: 31 August 2021

The adsorption isotherm reflects the relationship between the equilibrium concentration (C_e) and the equilibrium adsorption capacity (q_e) of the adsorbate in the solution when the adsorption reaches equilibrium under certain temperature conditions [18]. The change law of adsorption isotherms can help us analyze the interaction between adsorbate and adsorbent and the structural characteristics of the adsorption layer [19]. With the increase of the initial concentration, the adsorption capacity of TC in the saline soil increased. The higher the TC concentration, the greater the concentration gradient formed by the solid-liquid interface between TC and biochar, the greater the driving force for mass transfer caused by the concentration difference, and the greater the amount of TC adsorbed on the biochar surface [20]. In addition, the greater the TC concentration, the higher the probability of TC capture by biochar. Zhang et al. [18] put forward this point of view when studying TC adsorption by cow manure biochar. The amount of TC adsorption [Soil (0-20cm)>S(20-40cm)>S(40-60cm)] decreases with the increase of soil depth, which is closely related to the physical and chemical properties of the profile soil. Surface soil produces greater agricultural production disturbance, with high organic matter content, strong adsorption capacity, while great salt ion content of deep soil hinders adsorption. For soil with high clay content, its loose intergranular and aggregated structure and porous properties provide a larger specific surface area, a larger number of adsorption sites, which is more conducive to adsorption [21]. The surface of soil-like clay minerals is characterized by negative charges, and the positive charges in TC molecules can be adsorbed to the soil surface through cation exchange, which can also bond with the soil through cation bond bridging [22].

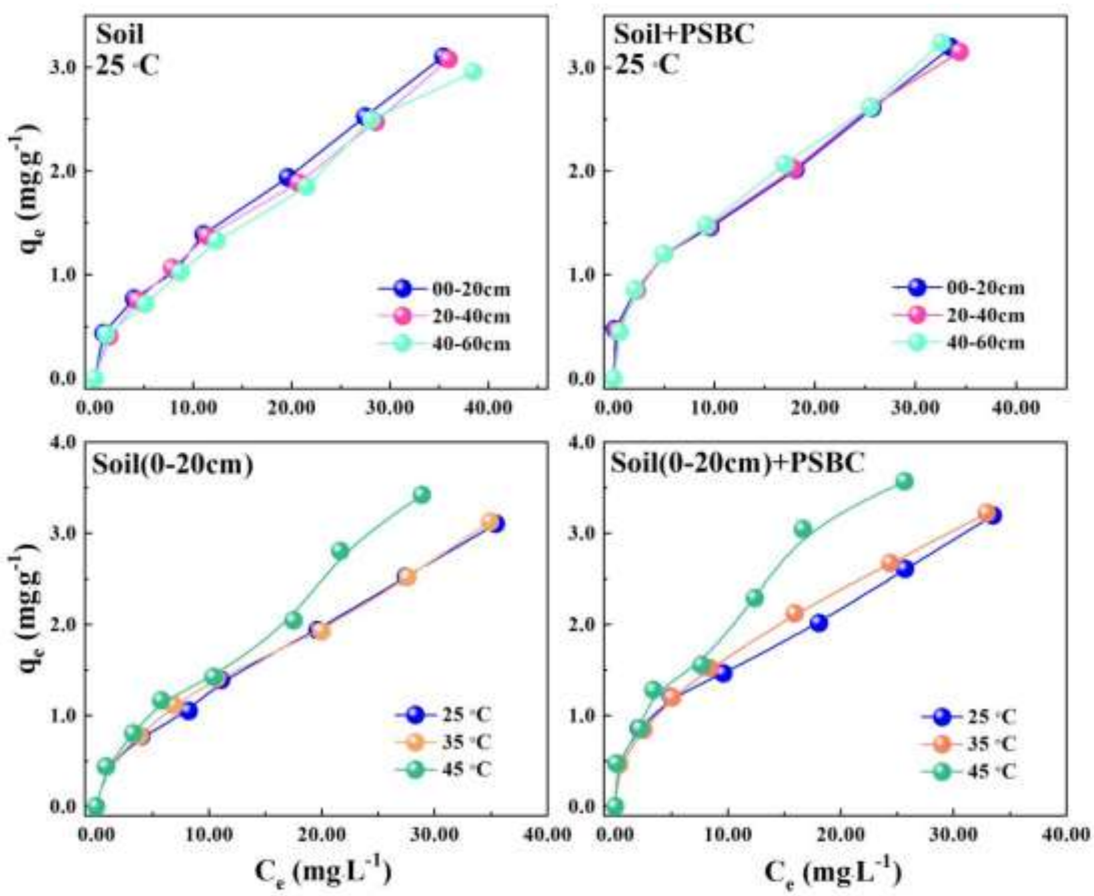

Fig 4: Adsorption isotherms of tetracycline adsorption by saline soil at different depths

Carboxyl groups in antibiotic molecules bond with oxygen atoms on the clay mineral surface to form hydrogen bonds, which may be one of the primary mechanisms of TC adsorption by soil. Antibiotics may also undergo hydrogen bonding before adsorption by interacting with polar functional groups in soil organic matter (especially the carboxyl groups, carbonyl, amine and methoxy groups in humic acids) [23]. Ion exchange and complexation reactions on metal oxides also play a role to a certain extent, while soil colloid migration greatly affects the adsorption behavior of antibiotics on soil [24]. The addition of cow manure biochar changed the adsorption characteristics of saline soil. After addition of cow manure biochar, the adsorption capacity of deep saline soil with the lowest organic matter content (7.23 g/kg) was significantly increased, which was higher than that of surface soil (10.10 g/kg). It is possible that the low organic content may weaken the filling effect of the soil complex components on the biochar, thereby enhancing TC adsorption by the saline soil. In addition, as the soil depth increases, the content of soil sand particles also increases, which is unconducive to the formation and stability of soil colloids. Moreover, the cation exchange capacity also decreases, which is unconducive to soil adsorption. However, low soil colloid content has

Forest Chemicals Revew
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Article History: Received: 12 May 2021 Revised: 25 June 2021 Accepted: 22 July 2021 Publication: 31 August 2021

weakened effect on the surface properties of cow manure biochar. As a result, the adsorption tendency of the deep saline soil added with cow manure biochar is superior to the other two. Studies have shown that the enhancement of TC adsorption by biochar is not only related to surface adsorption and void filling mechanisms, but also closely related to functional groups such as hydroxyl and carboxyl groups on the biochar surface. For soil with high organic matter content, the complex composition of organic matter competes with TC adsorption. Wu et al., [25] studied the effect and mechanism of higher soil adsorption of cetirizine due to biochar. It also showed that dissolved organic matter and other components in the soil would block or compete with biochar adsorption site, which exerts a certain impact on the adsorption of pollutants.

TABLE IV. Fitting characteristic values of thermodynamic model regarding TC adsorption by saline soil

SAMPLE	LINEAR MODEL		LAMGMUIR MODEL			FREUNDLICH MODEL		
	K_{L1}	r_L^2	K_{L2}	q_{max}	r_L^2	n	K_F	r_F^2
SOIL(0-20CM)/25℃	0.0758	0.9967	0.0553	4.2070	0.8106	1.8801	0.4064	0.9700
SOIL(L0-20CM)+PSBC/25℃	0.0763	0.9876	0.1320	3.4423	0.8787	3.0432	0.8065	0.9380
SOIL(0-20CM)/35℃	0.0748	0.9919	0.0650	3.9936	0.8573	1.9004	0.4247	0.9823
SOIL(L0-20CM)+PSBC/35℃	0.0810	0.9773	0.1152	3.7300	0.9161	2.3496	0.6534	0.9783
SOIL(0-20CM)/45℃	0.1039	0.9869	0.0601	4.7483	0.7664	1.7176	0.4247	0.9773
SOIL(L0-20CM)+PSBC/45℃	0.1231	0.9656	0.1315	4.2608	0.8401	2.6337	0.8685	0.9195
SOIL(20-40CM)/25℃	0.0736	0.9933	0.0449	4.4924	0.8693	1.6082	0.3062	0.9951
SOIL(20-40CM)+PSBC/25℃	0.0747	0.9827	0.1187	3.5423	0.9032	2.4248	0.6488	0.9816
SOIL(40-60CM)/25℃	0.0693	0.9913	0.0422	4.4131	0.7930	1.7409	0.3293	0.9693
SOIL(40-60CM)+PSBC/25℃	0.0801	0.9822	0.1097	3.6969	0.9091	2.1142	0.5689	0.9913

K_d (L/g) is the distribution coefficient; Q m (mg/g) is the maximum sorption capacity; k_F ((mg $^{(1-n)}$ · L^n)/g) is the Freundlich sorption coefficient and n (dimensionless) is the degree of sorption non-linearity.

The adsorption isotherm process was used to investigate the adsorption of saline soil against TC and the influence of exogenous substances on adsorption. Linear model, Langmuir model, and Freundlich model were used to fit the isotherm adsorption data of TC on saline soil. The fitting results are shown in Table IV. Both the Linear adsorption model (R^2>0.966) and the Freundlich model (R^2>0.920) can well explain the TC adsorption process on saline soil. For

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
Article History: Received: 12 May 2021 Revised: 25 June 2021 Accepted: 22 July 2021 Publication: 31 August 2021

hydrophobic organic adsorption that obeys the Linear model, the adsorption capacity of the adsorbent depends on the organic pollutant concentration and the distribution coefficient K_d. Hydrophobic distribution is beneficial to the TC adsorption by saline soil. After addition of pig manure biochar, the distribution coefficient K_d of saline soil against TC is greater than that of original saline soil. The addition of cow manure biochar with larger specific surface area and rich pore structure effectively increases the affinity and adsorption capacity of the adsorbent. Under high temperature, the adsorption distribution coefficient is greater. The Freundlich adsorption model describes the heterogeneous adsorption behavior, i.e. the adsorption process of multi-molecular layers on the substance surface and adsorbent with uneven spatial distribution. The adsorption isotherms of TC in the saline soil system and the cow manure biochar system are more in line with the Freundlich isotherm adsorption model, indicating that the adsorption of TC in the saline soil system is multi-molecular adsorption and the adsorption surface is uneven. The non-linear index n reflects the strength of the adsorption capacity ($n>1$ indicates that the adsorption is easy; $n<1$ indicates that the adsorption is difficult to proceed). The n values in Table IV are all greater than 1, indicating that the adsorption is easy to proceed. K_f reflects the intensity of TC adsorption by saline soil. Its larger value indicates stronger adsorption effect. In Table IV, the K_f value of biochar-added saline soil is greater than that of original saline soil, indicating that biochar addition has a positive promoting effect on saline soil adsorption. The adsorption mechanisms may include cation exchange, π-π electron donor acceptor effect, hydrogen bonding, electrostatic interaction and surface complexation, etc. [26].

3.3 The Impact of Temperature

With the increase of temperature, the total adsorption amount increases in the original saline soil and the saline soil added with pig manure biochar (Figure 4). The higher adsorption temperature will increase the degree of surface activation of the saline soil system, increase the available active sites, enhance its surface adsorption. Accordingly, it is manifested that heating is beneficial to the adsorption. In addition, with the increase in temperature, the viscosity coefficient of water decreases, the diffusion rate of TC in water is faster, and the probability of TC collision with saline soil increases, thereby increasing the adsorption capacity.

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
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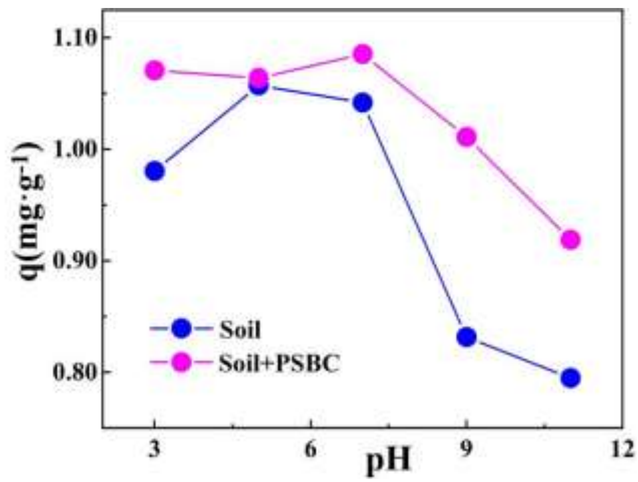

Fig 5: Change curve of tetracycline adsorption by saline soil under different pH

3.4 Effect of pH

Solution pH will change the properties of TC, saline soil and biochar, thereby affecting the adsorption strength of TC on it. pKa of TC is the main reason for changes of TC adsorption capacity under different pH. TC is an amphiphilic molecule with dissociation constants (pKa) of 3.3, 7.7, and 9.7, respectively. Under different environmental pH, TC can exist in the form of cations, zwitterions and anions. When the pH is 2, about 95% exists in the form of TCH_3^+; when the pH is 5, more than 95% exists in the form of TCH_2^0; when the pH is 7, about 75% exists in the form of TCH_2^0 and 25% exists in the form of TCH^-; when the pH is 9, about 70% exists in the form of TCH^- and 30% exists in the form of TC^{2-} [14]. As the solution pH increases from 3 to 11, the adsorption capacity of the original soil and the biochar-added saline soil against TC increases first and then decreases (Figure 5). When the solution pH is 3 ~7, the adsorption removal rate is above 80%. When the pH is 7, the adsorption capacity reaches the maximum, 1.05 mg/g and 1.08 mg/g respectively. Under acidic pH, TC exists in the form of cations and zwitterions. At this time, the soil organic components and the clay surface are mainly negatively charged, and electrostatic interactions greatly contribute to the adsorption capacity [27]. In addition, TC is easily hydrolyzed under acidic conditions, which can also react with functional groups such as -OH and $-NH_2$ on the adsorbent material surface [28]. Under lower pH, TC adsorption by biochar-added saline soil is significantly different from that by the original soil. Biochar has a large specific surface area, which may be the main reason for the enhanced surface adsorption. With the increase of pH, the adsorption capacity of saline soil and biochar–added saline soil against TC decreases continuously. This may be due to the strong electrostatic repulsion between negatively charged TC and saline soil, and weak π-π electron donor acceptor effect.

Forest Chemicals Revew
www.forestchemicalsreview.com
ISSN: 1520-0191
July-August 2021 Page No. 1595-1616
Article History: Received: 12 May 2021 Revised: 25 June 2021 Accepted: 22 July 2021 Publication: 31 August 2021

3.5 The Effect of Ionic Strength and Type on Adsorption

The natural environmental conditions are complex, and ions can accumulate in the saline soil system through a variety of ways, thereby affecting the environmental fate of TC [29]. The hydroxyl and benzene ring of TC can chelate with a variety of metal cations. At the same time, metal bridging is also one of the most important mechanisms in the adsorption process of antibiotics. Some ions can increase the adsorption coefficient of antibiotics on organic matter by several times [30], different cations have varying effects on soil adsorption of organic pollutants due to different competitive ability [31]. Figure 6 shows the effects of four common cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) on TC adsorption by the two adsorbents under different ionic strengths. When the ion concentration gradually increases, K^+ and Na^+ slightly inhibit TC adsorption by the two adsorbents, which is due to the increased salt in the soil, increased soil bulk density and decreased total porosity of the soil [32]. The divalent cations Ca^{2+} and Mg^{2+} display obvious inhibitory effects. On the one hand, Ca^{2+} and Mg^{2+} have higher charge numbers, showing much higher binding force with the two negatively charged adsorbents compared to K^+ and Na^+, and Ca^{2+} and Mg^{2+} adsorbed on saline soil bond with moisture to produce a hydration layer, which inhibits the contact and adsorption between the two adsorbents and TC [33]. On the other hand, Ca^{2+} and Mg^{2+} can bond with TC and occupy the adsorbable sites of TC. Compared with Ca^{2+}, Mg^{2+} has a smaller radius and stronger attraction to water molecules, which produces a thicker hydration layer. Under neutral conditions, Mg^{2+} can bond with more TC and occupy more adsorption sites, which therefore has greater inhibitory effect on adsorption than Ca^{2+}.

Forest Chemicals Revew
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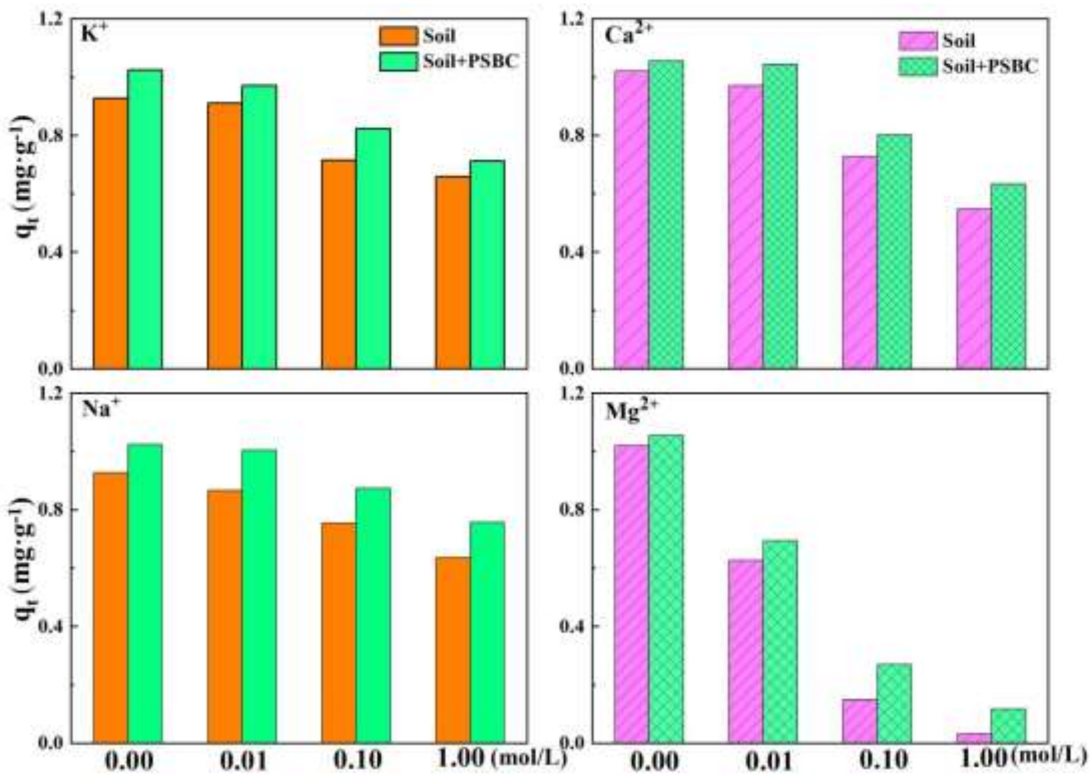

Fig 6: The effect of ion types on TC adsorption by saline soil

3.6 Analysis of Adsorption Mechanism

X-ray diffraction is a useful tool for expressing material crystallinity and determining fixed-form compounds [34]. In the study, PSBC and Soil+PSBC before and after the adsorption reaction were characterized by XRD, with the characterization results shown in Figure 7. According to the XRD image, PSBC and Soil+PSBC have sharp diffraction peaks before the adsorption reaction, which indicates higher crystallization of the adsorbent itself; Soil+PSBC diffraction peaks are sharper after adsorption, which indicates that Soil, Soil+PSBC maintain a high degree of crystallinity and shows a slight increase after adsorption. The diffraction peak of Soil+PSBC does not significantly shift after adsorption compared with the original sample, which further suggests that no fixed-form compound is formed on the Soil+PSBC surface after adsorption. The grain size of PSBC has not changed, which also reveals that TC adsorption on saline soil is affected by the physical adsorption mechanism. The kinetic process shows that adsorption is mainly affected by the chemical process. As a whole, it suggests that the adsorption process has both physical and chemical effects.

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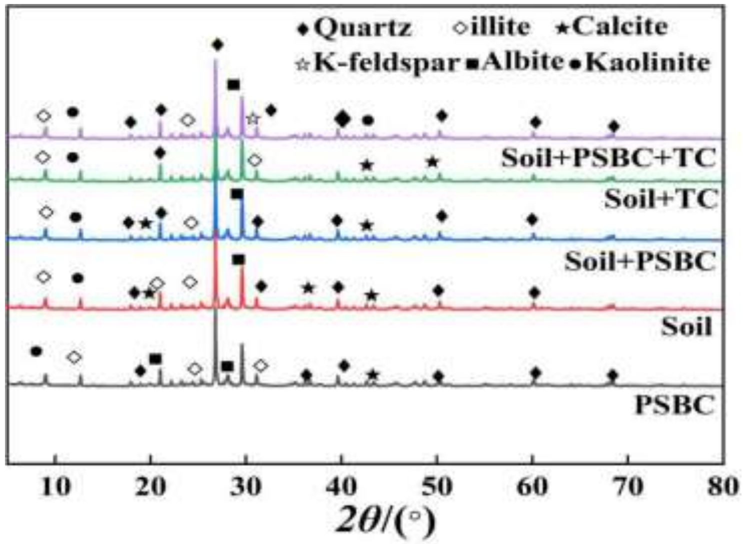

Fig 7: X-ray diffraction pattern of saline soil

Infrared spectroscopy is widely used for structural characterization before and after adsorption, and the surface functional groups can be qualitatively analyzed according to the infrared spectrogram of the adsorbent [35]. Figure 8 shows the infrared spectrogram of the saline soil system before and after TC adsorption. The wavelengths of pig manure biochar and saline soil added with pig manure biochar are basically similar after 1000/cm. At 528-620/cm and 665-860/cm, it is the absorption peak of iron and manganese oxide, which is significantly displayed in the saline soil system. Compared with the condition before TC adsorption, the absorption characteristic peaks of functional groups undergo different changes after TC adsorption by biochar-added saline soil, with weakened -OH stretching vibration peak at the wavelength 3422 cm^{-1}, and the corresponding $-CH_2$ elastic vibration at 1450/cm is also significantly weakened. It suggests that hydroxyl and alkyl groups play an important role in the adsorption process. The interaction between the saline soil system and TC molecules may cause changes in the hydrogen atom skeleton. The absorption peak at the wavelength of 1640/cm also exhibits significant changes, indicating the presence of π-π electron donor acceptor effect. At the same time, the absorption of C-O and C-O-C bonds is weakened at wavelength 1027 cm^{-1}. For its reason, the carboxyl and hydroxyl groups in the biochar can provide a large amount of H^+ which undergoes ion exchange reaction with TC in the solution. It further confirms that ion exchange takes place in this reaction. The absorption peaks of iron and manganese oxide are at 528-620/cm and 665-860/cm, and some of the absorption peaks are shifted after TC adsorption, with individual absorption peaks disappearing, indicating that iron and manganese oxides also participate in the TC adsorption process. Through the comparative analysis of XRD and FTIR before and after adsorption, it is shown that the adsorption of TC by the saline soil system involves a variety of adsorption mechanisms, as shown in Figure 9.

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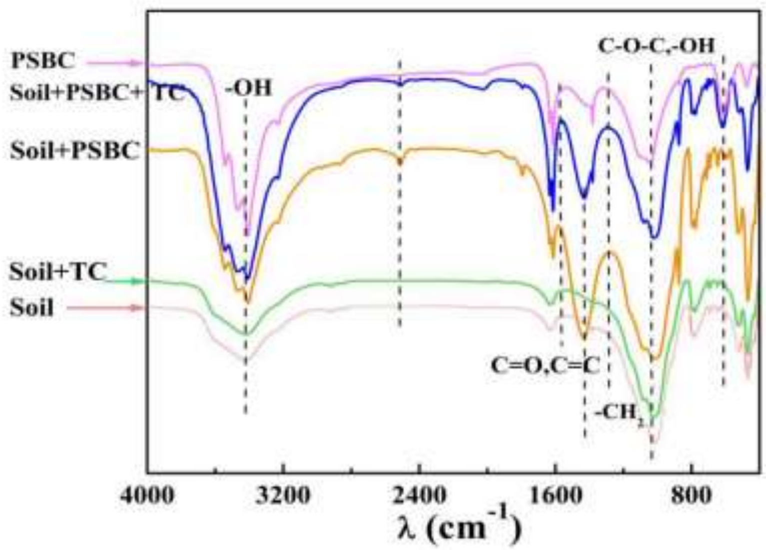

Fig 8: Infrared spectrogram of saline soil

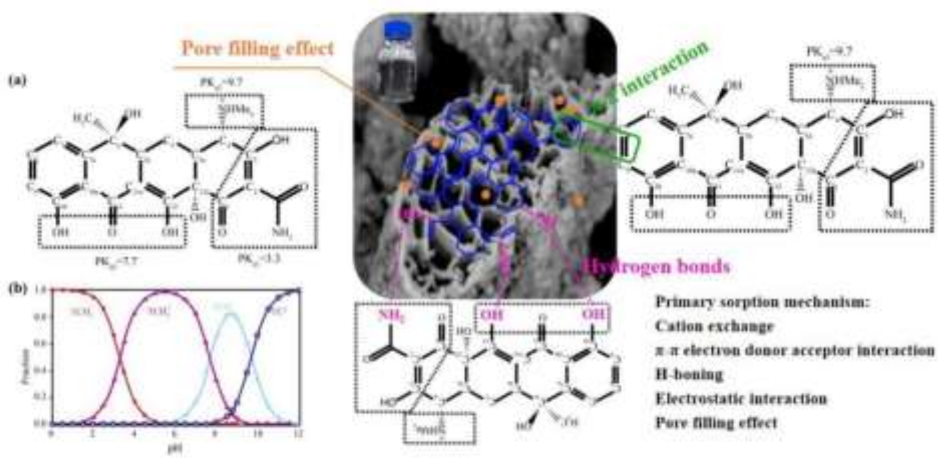

Fig 9: The main mechanism of TC adsorption by saline soil

IV. CONCLUSIONS

(1) The adsorption capacity of saline soil at different depths tends to increase with the extension of time, and the adsorption gradually reaches equilibrium after 360 min. The addition of biochar leads to the introduction of a large number of adsorption sites, which increases the surface adsorption and void filling capacity, but does not change the physical adsorption

process of saline soil. TC adsorption by saline soil added with pig manure biochar and original saline soil more accords with the quasi-second kinetic model.

(2) TC adsorption capacity decreases with the increase of soil depth, which is closely related to the physical and chemical properties of the profile soil. Surface soil produces greater agricultural production disturbance, with high organic matter content, strong adsorption capacity, while great salt ion content of deep soil hinders adsorption. The adsorption isotherm process conforms to the Linear and Freundlich models, and addition of biochar increases the adsorption distribution coefficient K_d of saline soil at different depths, with affinity enhanced.

(3) Increase in temperature is conducive to the adsorption. When pH is 7, the adsorption capacity reaches the maximum. K^+ and Na^+ slightly inhibit TC adsorption by saline soil, while divalent cations Ca^{2+} and Mg^{2+} significantly inhibit TC adsorption by saline soil.

(4) TC adsorption by saline soil has both physical and chemical effects, involving cation exchange, π-π electron donor acceptor effect, electrostatic interaction and void filling effect.

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