



Aging alters the physicochemical properties of biochar, enhances its adsorption performance for tris-(1-chloro-2-propyl) phosphate, and changes the adsorption mechanism

Qing Luo^{*}, Xinye Zhao, Yujie Li, Yongyao Deng, Qing He, Wenju Dai

Key Laboratory of Eco-restoration of Regional Contaminated Environment, Ministry of Education, Shenyang University, Shenyang 110044, China

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ABSTRACT

When introduced into the environment, biochar undergoes various aging processes, which can affect its ability to adsorb and immobilize pollutants. However, only a few reports exist regarding the effect of biochar aging on its ability to adsorb tris-(1-chloro-2-propyl) phosphate (TCIPP). Therefore, this study considers five near-natural aging processes (alternating dry-wet, alternating freeze-thaw, acid rain, microbial, and alternating dry-wet and freeze-thaw) to explore the impacts of biochar aging on its adsorption performance and mechanisms for TCIPP. The results indicate that following aging, the polarity of biochar undergoes a notable increase, while its aromaticity and hydrophobicity decrease notably. Additionally, the specific surface area decreases and the overall quantity of acidic oxygen-containing functional group increases significantly. These changes also alter the capability and underlying mechanisms of biochar in adsorbing TCIPP. Specifically, the highest adsorption capacities of biochar regarding TCIPP increase by 51.73 %, 80.59 %, 53.89 %, and 15.11 % after alternating dry-wet aging, microbial aging, alternating freeze-thaw aging, and alternating dry-wet and freeze-thaw aging, respectively. However, the maximum adsorption capacity decreases by 53.37 % after acid rain aging. Aging does not alter the types of interactions involved in the adsorption process of TCIPP by biochar, which include pore filling, hydrophobicity, hydrogen bonding, van der Waals forces, π - π interactions, pnicogen- π interactions, and more; however, it does change their intensities. This suggests that natural aging can enhance the capacity of biochar to adsorb TCIPP, thereby improving its effectiveness in remediating TCIPP-contaminated soil. This study provides a scientific rationale for utilizing biochar in the treatment of soil contaminated with TCIPP.

1. Introduction

Tris(1-chloro-2-propyl) phosphate (TCIPP) is an artificially synthesized phosphate derivative composed of three chlorinated propyl groups and one phosphate ester group. It is primarily used as a flame retardant in the production of strip and block foams, and it can also serve as a chemical intermediate for synthesizing other compounds with specific functionalities (van der Veen and de Boer, 2012). Especially after the manufacture and utilization of tris-(2-chloroethyl) phosphate (TCEP) were restricted due to its potential to cause kidney cancer, damage the nervous system and kidneys, and affect fertility, the production and usage of TCIPP, as its main substitute,

^{*} Corresponding author.

E-mail address: luoqingyt@126.com (Q. Luo).

rapidly increased, accounting for approximately 55 % of total organophosphorus flame retardants (van der Veen and de Boer, 2012; Wei et al., 2015). Nonetheless, TCIPP poses safety concerns. Research indicates that it has the potential to disrupt hormone levels in organisms, diminish the semen quality of adult males, and even trigger severe neurotoxicity and carcinogenic impacts (Huang et al., 2022; Yuan et al., 2024). Furthermore, TCIPP is incorporated into the final product through physical addition rather than chemical bonding, making it highly prone to escaping into the neighboring environment due to wear, leakage, and other means (Fan et al., 2014). Currently, TCIPP has been commonly identified in various environmental media such as air, water, soil, and sediments, and it is the most abundant OPE monomer in most environmental samples, with concentrations reaching up to 2500 $\mu\text{g}/\text{kg}$ (Lee et al., 2018; Luo et al., 2018, 2020; Wang et al., 2015). More importantly, TCIPP is not easily biodegradable (Luo et al., 2021). Therefore, there is a pressing need for the advancement of effective removal methods for TCIPP in various environmental matrices.

At present, methods such as hydrolysis, photodegradation, microbial degradation, phytoremediation, and adsorbent sorption are all being applied in study on the elimination of TCIPP in soil and water environments, with adsorbent sorption being considered the simplest and most effective approach (Fang et al., 2018; Yu et al., 2020; Qin et al., 2020; Liu et al., 2023; Luo et al., 2023 and 2024). In the field of contaminated soil remediation, biochar produced through biomass pyrolysis under limited oxygen conditions was regarded as an excellent adsorbent. It not only reduces the bioavailability of pollutants through sorption but also promotes the biodegradation of organic pollutants by microorganisms by improving the soil microenvironment (Liu et al., 2015; Zhang et al., 2018; Kong et al., 2018). Furthermore, our preliminary research has found that microbial degradation is the primary mechanism for TCIPP removal in soil (Luo et al., 2023). Therefore, using biochar for the restoration of soil contaminated with TCIPP should be an effective method. Our previous studies also indicate that corn straw-derived biochar exhibits favorable sorption capacity for TCIPP, and the higher the pyrolysis temperature during biochar preparation, the better its sorption performance for TCIPP. The highest sorption capacity for TCIPP of corn straw biochar produced at a pyrolysis temperature of 700 °C can reach 2.26 mg/g (Li et al., 2023a; Luo et al., 2024). However, once biochar enters the soil, it interacts with various soil components, leading to changes in its properties, such as surface morphology, physicochemical properties, and the types and contents of surface functional groups, which in turn affect its sorption efficiency for pollutants (Sorrenti et al., 2016; Rechberger et al., 2017). For example, Jin et al. (2017) found that nitric acid oxidation increases the aromaticity and hydrophilicity of biochar, leading to an augmentation in surface oxygen-containing functional groups. Grass straw biochar exhibited enhanced sorption capacity for phenanthrene, while the sorption effect of animal manure biochar on phenanthrene was relatively weakened. Ghaffar et al. (2015) discovered that nitric acid/sulfuric acid oxidation reduced the specific surface area of peanut shell-derived biochar and partially destroyed its pore structure, yet it enhanced its sorption capacity for dialkyl phthalates. However, there are also studies indicating that chemical aging weakens the π - π electron-donor-acceptor interaction between biochar and organic pollutants, thereby inhibiting the adsorption capacity of biochar (Liu and Chen, 2022). In short, the impact of aging on biochar's adsorption capacity varies based on several factors, such as the material used to make the biochar, pyrolysis temperature, aging method, and type of contaminant. Thus, to delve into the utilization potential of biochar in the restoration of TCIPP-contaminated soil, it is essential to elucidate how aging impacts biochar's ability to adsorb TCIPP.

The natural aging process of biochar is relatively slow, so artificial aging methods are often used to accelerate this process (Dong et al., 2017; He et al., 2019). Artificial aging mainly includes three methods: physical, chemical, and biological aging, among which chemical aging is the most commonly used (Liu and Chen, 2022). However, biochar that enters the soil undergoes aging due to the combined effects of multiple processes, including physical, chemical, and biological processes (Wang et al., 2020a). Therefore, the biochar produced from the pyrolysis of corn straw at 700 °C was selected as the raw biochar in this study. Five different aging methods, namely alternating dry-wet aging, alternating freeze-thaw aging, acid rain aging, microbial aging, and alternating dry-wet and freeze-thaw aging, were employed to simulate the potential natural aging process that may occur when biochar is added to the environment. The aim was to examine the alterations in the physicochemical properties of biochar under natural environmental conditions and their impact on the adsorption of TCIPP, to provide a foundational theory for utilization of biochar in actual soil environment.

2. Materials and methods

2.1. Materials and chemicals

The corn straw was gathered from Chaoyang City, Liaoning Province, and then cleaned with deionized water to get rid of surface dust and impurities. Following cleaning, the corn straw was dried overnight in an oven at 75 °C and then pulverized using a grinder. TCIPP standard sample (purity 99.5 %) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). HNO_3 , H_2SO_4 , and other chemicals were all obtained from Sinopharm (Shanghai, China). The deionized water used in the experiment was produced by Millipore (18.2 M Ω -cm, Billerica, MA, USA).

2.2. Preparation of biochar

The crushed corn straw was then poured into a crucible and exposed to oxygen-limited pyrolysis in a muffle furnace at 700 °C for 6 h. Once cooled to ambient temperature, the gathered solid particles were crushed and filtered through a 100-mesh sieve for future use (denoted as CS700).

Alternating dry-wet aging: Weigh out 5 g of biochar and place it in a 100 mL beaker. Add deionized water to the beaker containing the biochar, with the amount determined by weighing, to ensure that the water holding capacity of the biochar is 100 %. Then, place the beaker with biochar and water in a constant temperature drying oven and incubate it at 25 °C for 16 h, followed by 8 hours at 60 °C.

This constitutes one cycle. After completing 25 cycles of incubation, rinse and filter the biochar three times with deionized water, followed by freeze-drying and sieving through a 100-mesh screen for future use. (denoted as CS700-D).

Alternating freeze-thaw aging: Weigh out 5 g of biochar and place it in a 100 mL beaker. Add deionized water to the beaker containing the biochar, with the amount determined by weighing, to ensure that the water holding capacity of the biochar is 100 %. Then, transfer the beaker with biochar and water in a constant temperature drying oven and incubate it at 25°C for 19 h. Subsequently, place it in a refrigerator at −20°C for cultivation for 5 h. This constitutes one cycle. After completing 25 cycles of incubation, rinse and filter the biochar three times with deionized water, followed by freeze-drying and sieving through a 100-mesh screen for future use (denoted as CS700-F).

Simulated acid rain aging: Weigh out 5 g of biochar and place it in a 500 mL beaker. Add 400 mL of a mixed acid solution with a concentration of 20 %, which is prepared by mixing nitric acid and sulfuric acid in a volume ratio of 1:3. Then, transfer the beaker with biochar and acid solution in a constant temperature drying oven and incubate it at 20°C for 25 d. After the incubation is completed, rinse and filter the biochar repeatedly with deionized water until the pH value of the filtrate stabilizes. Followed by freeze-drying and sieving through a 100-mesh screen for future use (denoted as CS700-A).

Microbial aging: Weigh out 5 g of biochar and place it in a 250 mL flask. Add 25 mL of microbial inoculum and 25 mL of nutrient solution mix thoroughly, and then place the beaker in a 30°C incubator with shaking at 150 rpm for 14 d. Periodically add deionized water to ensure that the volume of liquid in the beaker remains at approximately 50 mL throughout the entire cultivation process. After the incubation is completed, rinse and filter the biochar repeatedly with deionized water until the OD_{600} value of the filtrate stabilizes, followed by freeze-drying and sieving through a 100-mesh screen for future use (denoted as CS700-M). The microbial inoculum was extracted from the soil (10–15 cm layer) of farmland located in Dadong District, Shenyang, Liaoning, China. Weigh 30 g of freshly collected soil and place it into a 250 mL flask. Add 60 mL of deionized water, and incubate with shaking at 60 rpm for 24 h. Afterward, obtain the microbial inoculum by filtering through filter paper. The nutrient solution is a mixture of glucose (6.38 g/L), NH_4Cl (40.66 g/L), KH_2PO_4 (4.67 g/L), peptone (10 mg/L), $CaCl_2$ (24 mg/L), $MnSO_4$ (4 mg/L), $ZnCl_2$ (4 mg/L), $CuSO_4$ (4 mg/L), and $MgCl_2$ (16 mg/L).

Alternating dry-wet and freeze-thaw aging: Weigh out 5 g of biochar and place it in a 100 mL beaker. Add deionized water to the beaker containing the biochar, with the amount determined by weighing, to ensure that the water holding capacity of the biochar is 100 %. Then, place the beaker with biochar and water in a constant temperature drying oven and incubate it at 60°C for 24 h. This process was carried out three times. Then, transfer the beaker containing biochar with a water holding capacity of 100 % to a refrigerator set at −20°C and incubate it for 24 h. Subsequently, thaw it at room temperature. Repeat this process three times. The aforementioned processes constitute one cycle. After completing 3 cycles of incubation, rinse and filter the biochar three times with deionized water, followed by freeze-drying and sieving through a 100-mesh screen for future use (denoted as CS700-DF).

2.3. Characterization of biochar

The SEM (S4800, Japan) was utilized to monitor the alterations in surface morphology of the biochar, both before and after the aging process. A specific surface area and pore size analyzer (JW-BK122F, China) was employed to measure the specific surface area and assess the pore size distribution of the biochar, both in its pre-aged and post-aged states. The C, H, and N element contents of the biochar before and after aging were measured using an element analyzer (Vario EL cube, Germany). The ash content was derived from the weight reduction observed after incinerating the biochar at 800°C for a duration of 4 h. The O content was determined through mass difference subtraction. The pH value was indicative of the solution formed by combining biochar with deionized water in a 1 (g): 20 (mL) ratio. The Boehm titration method was used to quantitatively measure and analyze the number of functional groups on the biochar, both in its pre-aged and post-aged states. The surface crystal structure of the biochar, both in its pre-aged and post-aged states, was characterized using XRD (UltimaIV, Japan). FTIR (IRTracer 100, Japan) was employed to detect the types and changes of surface functional groups on the biochar, both in its pre-aged and post-aged states, as well as after adsorbing pollutants. XPS (Escalab 250Xi, America) was utilized to examine the elemental makeup and chemical states of the biochar before and after aging, as well as after adsorbing pollutants.

2.4. Batch adsorption experiments

Individually weigh out 4 mg of biochar and introduce it into 8 mL of TCIPP solution, which has a mass concentration spanning from 50 to 1000 $\mu\text{g/L}$. Adjust the pH of the mixture solution to 7 using HCl or NaOH. Then, positions the mixture solution inside a temperature-controlled oscillating incubator maintained at 25 °C, and oscillates at a rotational speed of 120 r/min until a state of equilibrium is reached. Following performing filtration through a nylon membrane filter with a 0.22 μm pore size, utilize a UPLC-MS/MS method to directly determine the TCIPP concentration in solution (Luo et al., 2024). Each experimental run is replicated three times to ensure accuracy. Additionally, a control experiment is conducted in the absence of biochar. The control experiment demonstrated that the recovery rate of TCIPP exceeded 94 %, implying that the reduction of TCIPP in the solution during the experiment was due to the adsorption by biochar, rather than other factors.

2.5. Model fitting

The formula below is used to calculate the capability of biochar to adsorb TCIPP.

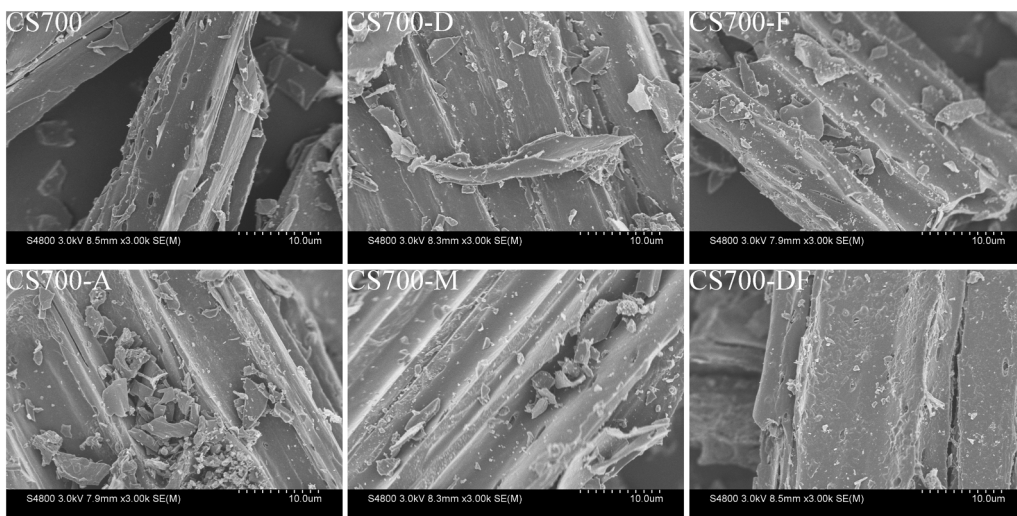


Fig. 1. The SEM photographs of biochar, both in its pre-aged and post-aged states ($\times 3000$).

Table 1

The physico-chemical characteristics of biochar before and after aging.

Biochar		CS700	CS700-D	CS700-F	CS700-A	CS700-M	CS700-DF
Element mass percentage	C (%)	80.58	75.61	78.46	70.91	77.44	75.34
	H (%)	1.21	1.66	1.85	2.73	1.75	1.49
	N (%)	1.35	1.51	1.33	1.37	1.34	1.56
	O (%)	9.20	13.58	11.21	22.36	11.97	13.27
Atomic ratio	H/C	0.017	0.020	0.017	0.019	0.017	0.021
	O/C	0.114	0.180	0.143	0.315	0.155	0.176
	(O+N)/C	0.129	0.202	0.166	0.354	0.177	0.196
	Ash (%)	7.67	7.64	7.16	2.63	7.51	8.34
pH		10.66	8.46	9.00	4.67	8.20	8.33
Specific surface area(m ² /g)		435.6	419.7	415.1	419.4	419.9	384.6
Pore volume (cm ³ /g)		0.258	0.248	0.247	0.262	0.247	0.232
Average pore size (nm)		2.37	2.36	2.38	2.50	2.35	2.42

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where Q_e is the capability of biochar to adsorb TCIPP at the equilibrium state (mg/g); Respectively, C_0 and C_e represent the starting and steady-state concentrations of TCIPP in the solution (mg/L); V denotes the solution's volume (L); m represents the biochar's mass (mg).

The adsorption procedure of biochar for TCIPP was fitted using the Langmuir, Freundlich, and Temkin models, respectively.

$$\text{Langmuir : } Q_e = \frac{Q_{\max} k_L C_e}{1 + k_L C_e} \quad (2)$$

$$\text{Freundlich : } Q_e = k_F C_e^{\frac{1}{n}} \quad (3)$$

$$\text{Temkin : } Q_e = \ln k_T + \ln C_e \quad (4)$$

Where $Q_{\max}$ denotes the max adsorption capacity (mg/g); Respectively, K_L (L/g) and K_F [(mg/g)·(L/g)^{1/n}] denote the adsorption constants of Langmuir and Freundlich; n denotes the Freundlich equilibrium parameter; K_T represents a constant that is associated with bond energy; a is the Kelvin temperature.

3. Results and discussion

3.1. Effect of aging on the properties of biochar

3.1.1. Surface morphology

The SEM images of biochar, both in its pre-aged and post-aged states are shown in Fig. 1, revealing notable variations in the

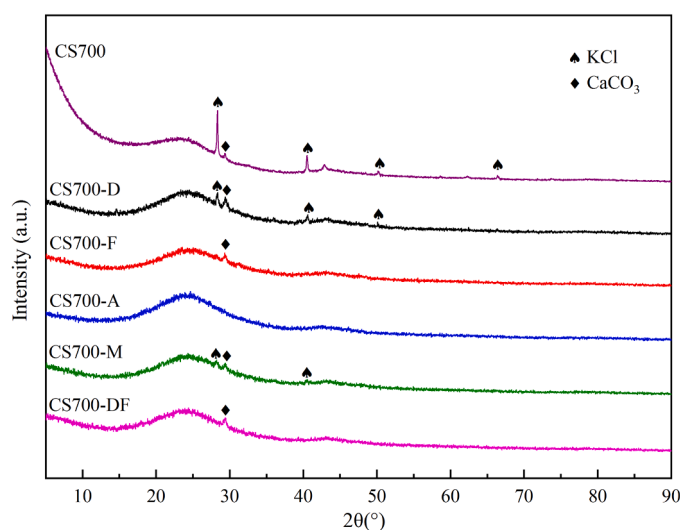


Fig. 2. The XRD patterns of biochar, both in its pre-aged and post-aged states.

biochar's surface structure subjected to various aging methods. As observed, the original biochar exhibits a smooth tubular structure with numerous unevenly distributed pores. These pore structures not only provide a favorable living environment for microbial activities but also constitute a crucial factor in the biochar's strong adsorption capacity as an adsorbent material (Chen et al., 2012). After aging, the micro-morphology of the biochar undergoes substantial changes, with localized areas showing varying degrees of damage, pore wall collapse, and increased surface roughness. Comparable findings were observed in the experimental results of Li et al. (2024). Among these, acid rain aging exerts the most prominent effect on the biochar's surface structure, resulting in the appearance of numerous particulate and bulk fragments on its surface. This often results in the obstruction of adsorption sites present on the biochar's surface, subsequently affecting its adsorption capacity for pollutants (Meng et al., 2020).

3.1.2. Elemental makeup and specific surface area

The fundamental physicochemical characteristics of biochar before and after aging are shown in Table 1. According to the table, after aging, the C content on the surface of biochar diminished significantly, while the O content rose markedly, with relatively minor changes in the contents of H and N. This may be due to the loss of labile carbon on the biochar surface under the influence of factors such as temperature, moisture, and microorganisms during aging, resulting in a reduction in C content (Li et al., 2024). Meanwhile, the biochar undergoes oxidation during aging, forming more oxygen-containing functional groups, thereby increasing the O content (Trompowsky et al., 2005). Compared with the original biochar, the C content on the surface of aged biochar diminished by 4.97 % (CS700-D), 2.12 % (CS700-F), 9.67 % (CS700-A), 3.14 % (CS700-M), and 5.24 % (CS700-DF), respectively, while the O content rose by 4.38 % (CS700-D), 2.01 % (CS700-F), 13.16 % (CS700-A), 2.77 % (CS700-M), and 4.07 % (CS700-DF), respectively. In other words, for the elemental composition of biochar, acid rain aging had the greatest impact, followed by alternating dry-wet aging and alternating dry-wet and freeze-thaw aging. The impacts of microbial aging and alternating freeze-thaw aging were relatively minor.

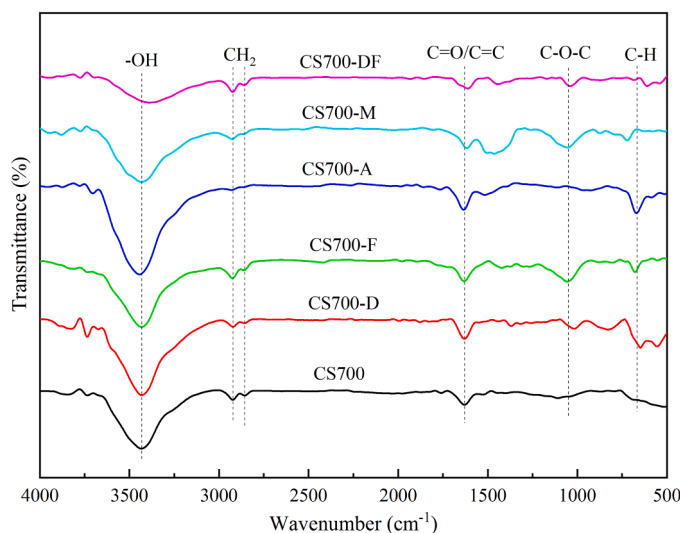
The ratios of hydrogen to carbon (H/C), oxygen to carbon (O/C), and the total of oxygen and nitrogen ((O+N)/C) in biochar can be used to characterize its aromaticity, hydrophilicity, and polarity, respectively. A decreased H/C ratio signifies a greater degree of aromatization within the biochar, whereas elevated O/C and (O+N)/C ratios imply a greater affinity for water and polarity of the biochar (Chen and Chen, 2009; Wiedner et al., 2013). After aging, the H/C ratios of biochar increased slightly, but the O/C and (O+N)/C ratios increased to a certain extent. Among them, the impact of acid rain aging was the most significant, with the O/C and (O+N)/C ratios increasing by 2–3 times. Following that, in order of significance, were alternating dry-wet aging, alternating dry-wet and freeze-thaw aging, microbial aging, and alternating freeze-thaw aging. These suggest that the process of aging diminishes the aromatic character and hydrophobicity of biochar while increasing its polarity, which is consistent with the findings of Cheng and Lehmann (2009).

After aging, the pH values of biochar undergo a notable reduction. Specifically, biochar subjected to acid rain aging changed from alkaline to acidic, with the pH value dropping from 10.66 to 4.67. In contrast, biochar aged by other methods remained alkaline, with pH values decreasing to between 8 and 9. This could be attributed to the rise in acidic oxygen-containing functional groups present on the biochar surface after aging (Wang et al., 2017). The increase in O content after aging, especially the significant increase after acid rain aging, serves as evidence of this. The impact of different aging methods on the ash content of biochar varies. Acid rain aging significantly reduces the ash content of biochar, which may be due to the dissolution and loss of inorganic components in biochar readily caused by the strong oxidation of concentrated acids such as $\text{HNO}_3/\text{H}_2\text{SO}_4$ (Chang et al., 2019). After alternating dry-wet aging, microbial aging, and alternating freeze-thaw aging, the ash content of biochar does not change significantly. However, alternating dry-wet and freeze-thaw aging increased the ash content. Some components that are resistant to ashing may have adsorbed some stable elements during the processes of dry-wet and freeze-thaw aging, thereby increasing the ash content (Cao et al., 2019).

Table 2

The content of functional groups present on biochar's surface before and after aging.

Biochar	Alkaline functional groups (mmol/g)	Acidic oxygen-containing functional groups (mmol/g)				
		-COOR	-C=O	-COOH	-OH	Total
CS700	0.17	0.06	0.24	0.08	0.11	0.49
CS700-D	0.13	0.07	0.27	0.09	0.20	0.63
CS700-F	0.16	0.08	0.31	0.05	0.15	0.59
CS700-A	0.07	0.12	0.25	0.27	0.47	1.11
CS700-M	0.12	0.09	0.41	0.09	0.12	0.71
CS700-DF	0.09	0.11	0.32	0.11	0.09	0.63

**Fig. 3.** The FTIR spectra of biochar, both in its pre-aged and post-aged states.

After aging, the total pore volume and average pore diameter of biochar do not change significantly. However, there is a certain degree of decrease in the specific surface area. In particular, alternating dry-wet and freeze-thaw aging results in the largest reduction in specific surface area, decreasing from 435.6 to 384.6 m²/g. The impact of alternating dry-wet aging, microbial aging, alternating freeze-thaw aging, and acid rain aging on the specific surface area of biochar is similar in degree. The decrease in specific surface area is caused by the localized fractures and fragmentation of the biochar surface due to aging (Ghaffar et al., 2015; Mia et al., 2017), as can also be observed from the scanning electron microscope images of the biochar.

3.1.3. Crystal structure

The XRD spectra of biochar under different aging treatments are shown in Fig. 2. The original biochar is rich in KCl crystal diffraction peaks located at $2\theta = 28.35^\circ, 40.52^\circ, 50.19^\circ$, and 66.40° , respectively, and there is also a diffraction peak of CaCO₃ crystals at $2\theta = 29.48^\circ$ (Liu et al., 2020). Aging significantly reduces the KCl crystal content in biochar. Among them, the effects of alternating freeze-thaw aging, acid rain aging, and alternating dry-wet and freeze-thaw aging are the most pronounced, resulting in the complete disappearance of KCl crystals in biochar, followed by microbial aging and alternating dry-wet aging. This phenomenon has also been observed in other studies on biochar aging, primarily due to KCl being easily soluble in water (Tan et al., 2020). Conversely, due to the low solubility of CaCO₃ in water, there is virtually no change in the CaCO₃ crystals in biochar after undergoing alternating dry-wet aging, alternating freeze-thaw aging, microbial aging, and alternating dry-wet and freeze-thaw aging. However, after acid rain aging, the CaCO₃ crystals in biochar disappeared, which may be due to the destruction of the crystal structure on the biomass surface under the effect of acid rain aging, resulting in a decrease in the crystallinity of the biochar (Liu et al., 2021).

3.1.4. Surface functional group content

The quantities of surface functional groups present on biochar subjected to different aging treatments are shown in Table 2. As can be seen from the table, the contents of alkaline and acidic functional groups in the original biochar are 0.17 and 0.49 mmol/g, respectively, significantly lower than those of the alkaline (1.07 mmol/g) and acidic oxygen-containing functional group contents (0.94 mmol/g) in the corn straw biochar pyrolyzed at 400°C by Wang et al. (2018). This may be related to the conditions used in the production of biochar, including the pyrolysis temperature. Our previous research indicates that a higher pyrolysis temperature significantly reduces the content of acidic oxygen-containing functional groups, decreasing from 1.02 mmol/g at 350°C to 0.49 mmol/g at 700°C (Luo et al., 2024).

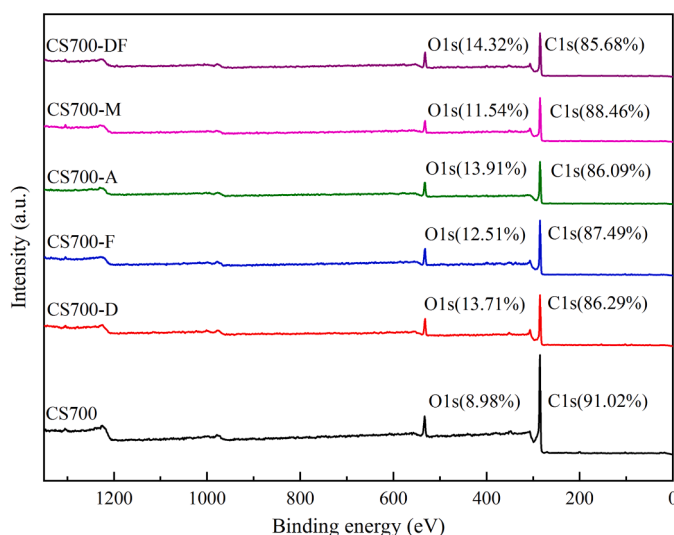


Fig. 4. The XPS full spectrum of biochar, both in its pre-aged and post-aged states.

Aging increases the quantity of acidic oxygen-containing functional groups and decreases the quantity of alkaline functional groups. This is consistent with the decrease in the pH value of aged biochar. Specifically, alternating dry-wet aging, acid rain aging, alternating freeze-thaw aging, microbial aging, and alternating dry-wet and freeze-thaw aging respectively increased the acidic oxygen-containing functional groups by 0.14 mmol/g, 0.62 mmol/g, 0.10 mmol/g, 0.22 mmol/g, and 0.17 mmol/g, while decreasing the alkaline functional groups by 0.04 mmol/g, 0.10 mmol/g, 0.01 mmol/g, 0.05 mmol/g, and 0.08 mmol/g. Among these, acid rain aging exerts the greatest influence on the alterations in the quantity of acidic and alkaline functional groups on the biochar's surface. This is consistent with the results of some previously reported studies (Wang et al., 2018; Zhao et al., 2020).

Further analysis reveals that the effects of different aging methods on various acidic oxygen-containing functional groups are also dissimilar. Acid rain aging had the greatest impact on the variation in the lactone group (-COOR) content. For phenolic hydroxyl groups (-OH), acid rain aging (with the largest content variation) and alternating dry-wet and freeze-thaw aging (with content reduction) exhibited the most significant effects. Alternating freeze-thaw aging (with content reduction) and acid rain aging (with the largest content variation) had the most pronounced impacts on carboxyl groups (-COOH). As for carbonyl groups (-C=O), microbial aging had the greatest influence on their content variation.

3.1.5. FTIR

Fig. 3 displays the FTIR spectroscopy of biochar, comparing its state before and after aging. The figure illustrates the existence of diverse functional groups on the biochar's surface, including carbon-carbon double bonds, carbon-oxygen double bonds, carbonyl groups (C=O), hydroxyl groups (-OH), and ester groups (C-O-C) (Mia et al., 2017). After aging, corresponding changes occurred in the chemical bonds or functional groups on the biochar's surface, which is in agreement with the findings of Chen et al. (2016). However, these changes only manifest in the peak intensities, with no alteration in their positions, suggesting that aging merely alters the content of the surface functional groups on the biochar without changing their types. Specifically, alternating dry-wet aging, acid rain aging, microbial aging, and alternating freeze-thaw aging increase the vibration intensity of -OH (3432 cm^{-1}) on the biochar surface, while alternating dry-wet and freeze-thaw aging decreases it. This is consistent with the results of Boehm titration. This suggests that aging alters the carbohydrates present on the biochar surface (Li et al., 2023b). Alternating freeze-thaw aging, alternating dry-wet aging, and alternating dry-wet and freeze-thaw aging increase the vibration intensity of -CH_2 (2924 cm^{-1} and 2855 cm^{-1}) on the biochar surface, while acid rain aging and microbial aging decrease it. This indicates that the content of aliphatic substances on the biochar's surface changes throughout the aging process (Tang et al., 2021). Aging results in a significant enhancement of the stretching vibration peaks of C=C/C=O, C-O-C, and C-H on the biochar surface, suggesting that oxidation reactions occur during the aging process. This is consistent with the results of both elemental analysis and Boehm titration. The amounts of oxygen-containing functional groups present on the biochar's surface increased, which can provide more binding sites for the adsorption process of contaminants on the biochar and enhance its adsorption performance for pollutants (El-Hendawy, 2003; Liu et al., 2013).

3.1.6. XPS

The XPS full spectra of biochar, both in its pre-aged and post-aged states are illustrated in Fig. 4. It is evident from the figure that the major elements on the biochar's surface remain unchanged before and after aging. The peak for C1s is situated at 284.8 eV, while the peak for O1s is positioned at 533.1 eV. However, aging altered the intensity of the C1s and O1s spectral peaks in the surface functional groups of the biochar. Alternating dry-wet aging, alternating freeze-thaw aging, acid rain aging, microbial aging, and alternating dry-wet and freeze-thaw aging decreased the intensity of C1s spectral peak by 4.73 %, 3.53 %, 4.93 %, 2.53 %, and 5.34 %, respectively.

Table 3

The binding states and relative atomic percentages of C1s and O1s on the biochar surfaces, both before and after aging.

Line	Binding energy/eV	Chemical Bonds / Functional Groups	Atomic percentage/%					
			CS700	CS700-D	CS700-F	CS700-A	CS700-M	CS700-DF
C1s	284.8	C-C	75.25	67.90	68.32	63.14	69.40	67.39
	285.7	C-O	13.20	12.45	12.55	12.00	12.48	11.47
	287.0	C=O	6.16	9.21	12.01	14.04	11.05	12.94
	288.9	O=C-O	5.39	6.45	7.12	10.82	7.07	8.20
O1s	531.5	C=O	30.79	27.81	25.78	24.73	25.03	27.28
	532.3	O-H	34.30	36.05	38.14	36.49	37.25	31.88
	533.2	C-O-C	20.74	20.95	22.83	21.48	20.81	21.42
	534.2	C-OOH	14.17	15.19	13.25	17.29	16.91	15.42

Simultaneously, they also caused a corresponding increase in the intensity of the O1s spectral peak. This indicates that aging increases the content of oxygen-containing functional groups on the surface of biochar (Cui et al., 2021), which is consistent with the findings derived from elemental analysis, Boehm titration, and FTIR.

The characteristic peaks of C1s and O1s on the biochar before and after aging were separately subjected to peak fitting. The fitted C1s and O1s spectra, each consisting of four components, are presented in Fig.S1 and S2, respectively. The figures indicate that the carbon atoms on the biochar surface primarily occur in the form of C-C bonds hybridized as sp^2 and sp^3 , which represents the helical structure of the aromatic carbon and benzene rings (Wang et al., 2020b). The oxygen atoms are primarily present in the form of O-H groups. According to the binding energy, chemical bonds, and variations in atomic percentages of C1s and O1s on the biochar surface before and after aging (Table 3), all five aging processes led to a reduction in the proportion of C-C on the surface of the biochar. Among them, acid rain aging caused the most significant decrease in the proportion of C-C, from 75.25 % to 63.14 %, while the decrease observed in the other four aging methods was consistent. The decrease in the proportion of C-C indicates the destruction of aromatic structures in the biochar, resulting in a reduction in the aromaticity of the biochar (Cui et al., 2021). This is consistent with the results of elemental analysis. For O-H bonds, alternating dry-wet aging, alternating freeze-thaw aging, acid rain aging, and microbial aging increase its proportion, whereas combined alternating dry-wet and freeze-thaw aging decreases its proportion. This is consistent with the results of Boehm titration and FTIR. Hydroxyl (O-H) is mainly influenced by water molecules in the biochar (Wang et al., 2020b), indicating that aging alters the content of bound water in the biochar. Aging also significantly increased the proportion of O=C-O functional groups, with acid rain aging causing the largest increase, followed by alternating dry-wet and freeze-thaw aging, alternating freeze-thaw aging, microbial aging, and alternating dry-wet aging. The O=C-O functional group represents the ester group, its presence can enhance the hydrophilicity and polarity of the biochar surface (Wang et al., 2020b), indicating that aging can increase the ester group content of biochar, thereby improving its hydrophilicity and polarity. This is consistent with the results of elemental analysis. In general, after aging, the total amount of oxygen-containing functional groups of biochar increases, which is consistent with the results obtained from Boehm titration and FTIR.

3.2. Effect of aging on the performance of biochar in adsorbing TCIPP

To explore the mechanism by which biochar adsorbs TCIPP under different aging conditions, the adsorption results of biochar were modeled and analyzed utilizing the Langmuir, Temkin, and Freundlich models, respectively. As illustrated in Fig. 5, with the starting concentration of TCIPP rising, the biochar's adsorption capability for TCIPP substantially elevated ($P < 0.01$), ultimately leveling off and reaching an equilibrium state. The primary reason for this was that, at lower initial concentrations of TCIPP, the biochar's surface had an abundance of binding sites, which enabled swift adsorption of TCIPP. With the starting concentration of TCIPP progressively raised, the adsorption sites located on the biochar's surface progressively reached saturation, resulting in a slower increase in adsorption capacity (Chen et al., 2018).

As shown in Table 4, the process of TCIPP being adsorbed onto biochar, including the original biochar, biochar aged by alternating dry-wet, acid rain, and alternating freeze-thaw, fits better with the Temkin model, indicated by higher R^2 values. This suggests that surface adsorption is the primary adsorption process, with intermolecular forces also presented (Cui et al., 2020). In contrast, the adsorption process of biochar aged by microbial and alternating dry-wet and freeze-thaw is more reasonably explained by the Langmuir model, indicating that chemical adsorption plays a major role at this time (Fan et al., 2020). Compared to the original biochar, the maximum adsorption capacity of TCIPP onto biochar aged by alternating dry-wet, microbial, alternating freeze-thaw, and alternating dry-wet and freeze-thaw increased by 51.73 %, 80.59 %, 53.89 %, and 15.11 %, respectively. Aging, to a certain extent, enhanced the adsorption effect of biochar on TCIPP. However, the maximum adsorption capacity of TCIPP onto biochar decreased by 53.37 % after acid rain aging, indicating a weakened adsorption capacity. The order of improvement in biochar adsorption performance among the five aging treatments is: microbial > alternating freeze-thaw > alternating dry-wet > alternating dry-wet and freeze-thaw > acid rain.

The values of n and K_F within the Freundlich model can be used to assess the adsorption performance of biochar (Dong et al., 2011). The $1/n$ values for the adsorption of TCIPP onto biochar both in its pre-aged and post-aged states (ranging from 0.356 to 0.740) are all below 1, suggesting that the process of TCIPP being adsorbed onto aged biochar is readily occurring. The K_F values of biochar increased under alternating freeze-thaw aging, microbial aging, alternating dry-wet aging, and alternating dry-wet and freeze-thaw aging,

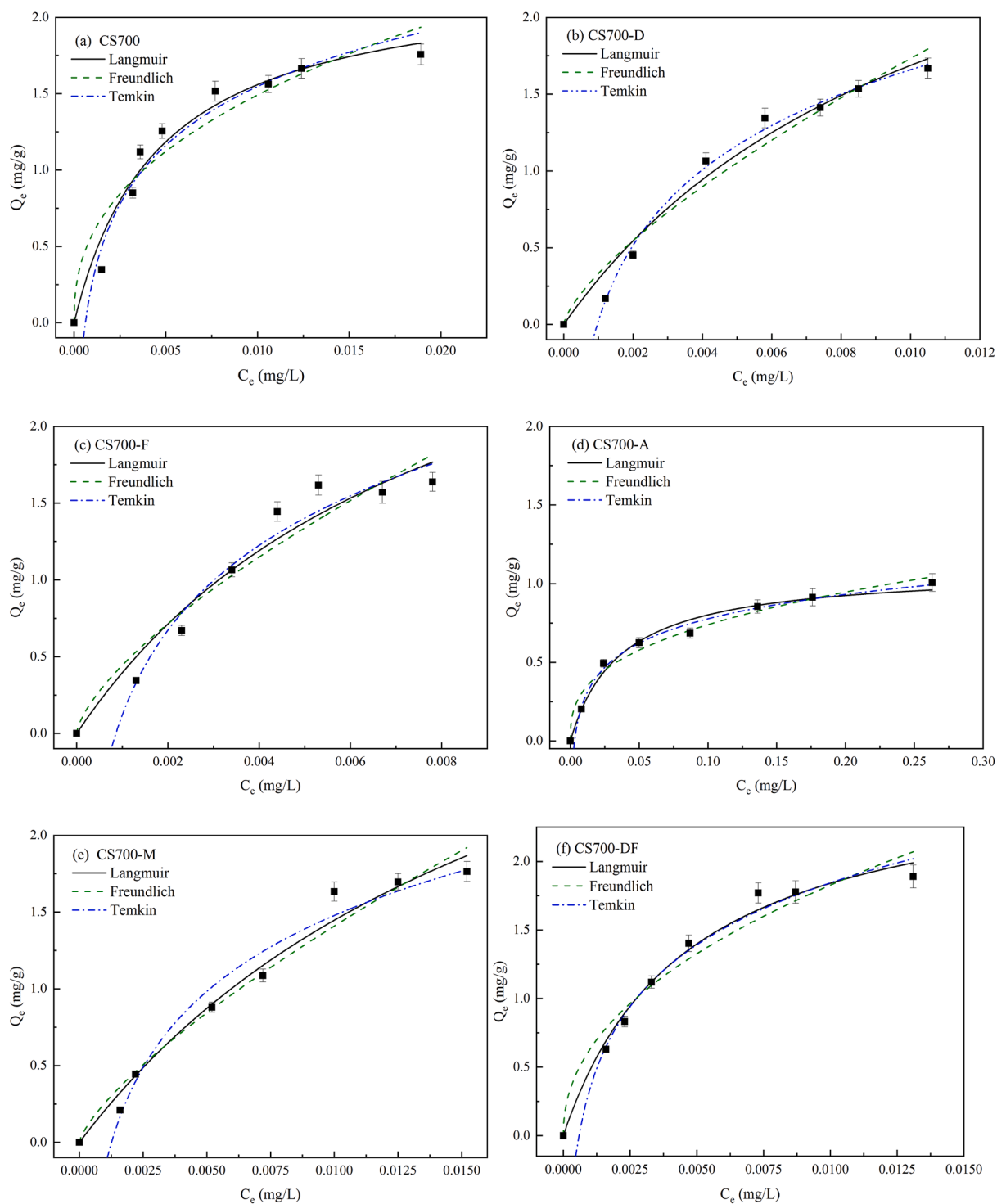


Fig. 5. The isotherm fitting curves for the adsorption of TCIPP by biochar, both in its pre-aged and post-aged states.

suggesting a significant enhancement regarding the adsorption performance of these aged biochars towards TCIPP. Conversely, the K_F value of biochar significantly decreased after acid rain aging, indicating a weakened adsorption capacity of the biochar after this type of aging (Liu et al., 2019; Xiang et al., 2020).

Table 4
Fitting parameters for isothermal adsorption of TCIPP by biochar before and after aging.

Biochar	Langmuir			Freundlich			Temkin		
	kL	Qm	R2	kF	n	R2	kT	a	R2
CS700	194.6	2.34	0.973	10.84	2.31	0.920	1459.4	0.573	0.973
CS700-D	90.46	3.55	0.973	47.16	1.39	0.95	1032.8	0.711	0.995
CS700-F	123.3	3.60	0.947	50.47	1.46	0.925	1164.4	0.796	0.967
CS700-A	27.59	1.09	0.982	1.68	2.81	0.977	324.9	0.223	0.993
CS700-M	52.03	4.23	0.978	45.51	1.35	0.966	793.2	0.714	0.975
CS700-DF	215.5	2.70	0.987	15.35	2.16	0.955	1692.1	0.652	0.985

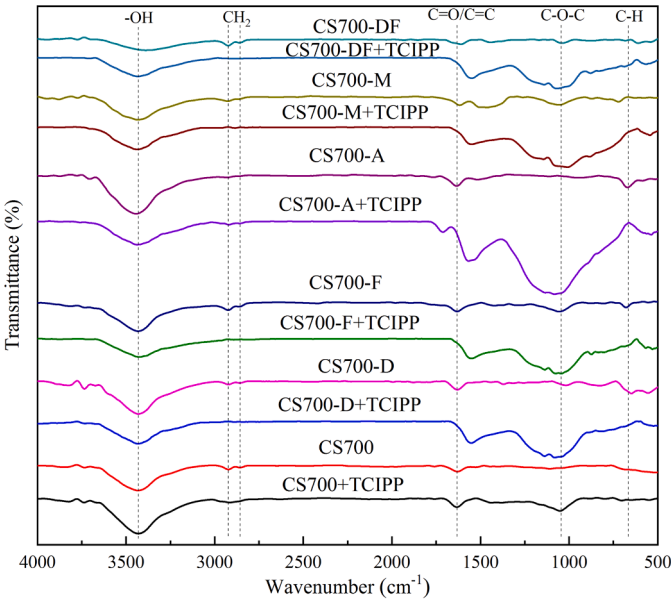


Fig. 6. The FTIR spectra of original and aged biochar, before and following adsorption of TCIPP.

3.3. Effect of aging on the mechanism of biochar adsorption for TCIPP

The primary mechanisms for the adsorption of organic pollutants by biochar encompass the partition effect and surface adsorption (Sivaranjanee et al., 2024). The nonlinear relationship observed in the isothermal adsorption curves of biochar indicates that surface adsorption plays a dominant role in the adsorption process of TCIPP by biochar. Research has shown that the surface adsorption of organic pollutants onto biochar involves both physical adsorption mechanisms (such as hydrophobic interactions, van der Waals forces, and electrostatic attraction) and chemical adsorption processes (including hydrogen bonding and π - π interactions) (Luo et al., 2022). Our previous research also indicated that the process of TCIPP being adsorbed by biochar involves pore-filling effects, hydrophobic interactions, hydrogen bonding, pnictogen- π interactions, and electrostatic attraction (Luo et al., 2024). In this study, aging significantly reduced the specific surface area of biochar, indicating a notable weakening of the pore-filling capability of aged biochar towards TCIPP. Additionally, aging decreased the aromatic nature and water-repelling properties of biochar, while increasing its polarity, suggesting a marked reduction in the hydrophobic interaction between aged biochar and the water-repelling organic contaminant TCIPP.

Further analysis of the FTIR (Fig. 6) before and after biochar adsorbing TCIPP reveals that after adsorbed TCIPP, there is a notable increase in the absorption peak intensity of -OH on the surface of the original biochar, suggesting that hydrogen bonding plays a role in the process of TCIPP adsorption by the original biochar (Rajapaksha et al., 2014). However, after TCIPP adsorption by aged biochar, the absorption peak intensity of -OH on the biochar surface exhibits different variation characteristics. Specifically, alternating dry-wet aging, acid rain aging, and alternating freeze-thaw aging weakened the absorption peak intensity of -OH, while microbial aging did not affect it. In contrast, alternating dry-wet and freeze-thaw aging enhanced the absorption peak intensity. This may suggest that chemical adsorption may be involved in the process of TCIPP adsorption by the aged biochar subjected to alternating dry-wet aging, acid rain aging, and alternating freeze-thaw aging. Hydrogen bonding may play a role in the TCIPP adsorption process by the aged biochar subjected to alternating dry-wet and freeze-thaw aging. Regardless of whether it is original or aging biochar, after adsorbed TCIPP, the intensity of the -CH₂ absorption peak on the biochar surface weakens or even disappears. This indicates that hydrophobic interactions and van der Waals forces may be involved in the process of TCIPP adsorption by biochar (Zhao et al., 2021), and aging does not alter

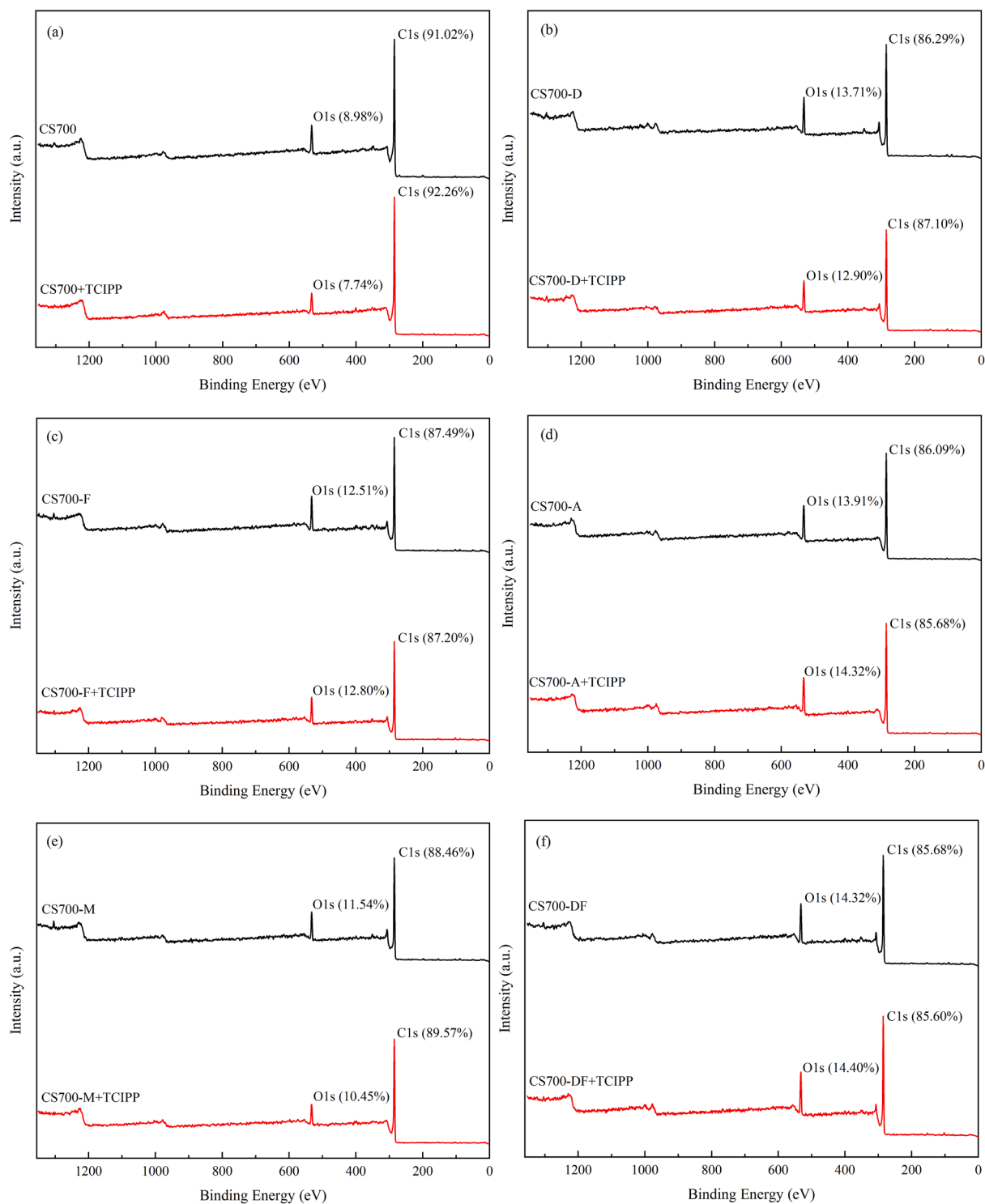


Fig. 7. The XPS spectra of original and aged biochar, before and following adsorption of TCIPP.

this interaction. Both original and aging biochar exhibit an increase in the absorption peak intensity of C-O-C groups on their surfaces after adsorbing TCIPP. The magnitude of this increase is significantly greater for aging biochar compared to original biochar. Among them, the increase is most pronounced for biochar aged by acid rain. However, neither surface adsorption nor partition effects typically enhance the C-O-C absorption peak intensity of biochar. The specific interaction responsible for this increase remains uncertain and

Table 5
Binding states and relative atomic percentages of C1s and O1s on the surface of original and aged biochar, before and following the adsorption of TCIPP.

Line	Binding energy/eV	Chemical Bonds / Functional Groups	Atomic percentage/%											
			CS700	CS700 +TCIPP	CS700-D	CS700-D+TCIPP	CS700-F	CS700-F+TCIPP	CS700-A	CS700-A+TCIPP	CS700-M	CS700-M+TCIPP	CS700-DF	CS700-DF+TCIPP
C1s	284.8	C-C	75.25	75.17	67.90	66.95	68.32	59.66	63.14	61.46	69.40	62.80	67.39	61.49
	285.7	C-O	13.20	11.56	12.45	11.70	12.55	11.43	12.00	10.92	12.48	11.67	11.47	10.48
	287.0	C=O	6.16	7.63	9.21	12.50	12.01	19.16	14.04	15.49	11.05	15.49	12.94	15.38
	288.9	O=C-O	5.39	5.64	6.45	8.85	7.12	9.75	10.82	12.13	7.07	10.04	8.20	12.65
O1s	531.5	C=O	30.79	32.28	27.81	29.80	25.78	26.31	24.73	25.84	25.03	26.11	27.28	29.29
	532.3	O-H	34.30	33.70	36.05	34.45	38.14	37.44	36.49	35.41	37.25	36.88	31.88	30.59
	533.2	C-O-C	20.74	21.96	20.95	21.45	22.83	24.07	21.48	22.66	20.81	20.83	21.42	24.48
	534.2	C-OOH	14.17	12.06	15.19	14.29	13.25	12.19	17.29	16.08	16.91	16.18	15.42	15.08

requires more detailed analysis in the future. After the adsorption of TCIPP, the absorption peak intensities of $\text{C}=\text{C}/\text{C}=\text{O}$ on the surfaces of both original and aged biochars changed, indicating that processes such as π - π interactions and hydrogen bonding may occur during the adsorption of TCIPP by biochar (Wang et al., 2020b). However, the absorption peak intensities of $\text{C}=\text{C}/\text{C}=\text{O}$ increased after TCIPP adsorption by original biochar, whereas they decreased or even disappeared after TCIPP adsorption by aged biochar. This may suggest differences in the strengths of π - π interactions and hydrogen bonding.

XPS full-spectrum (Fig. 7) reveals that the peak positions of C1s and O1s after TCIPP adsorption on aged biochar are 284.8 eV and 533.1 eV respectively, remaining unchanged compared to those before adsorption. By comparing and analyzing the peak intensities of C1s and O1s before and after TCIPP adsorption, it is found that the peak intensity of C1s on the biochar's surface increases following alternating dry-wet aging and microbial aging, with increases of 0.81 % and 1.11 % respectively, while a reduction in the peak intensity of O1s is noted. Conversely, the peak intensity of O1s on the biochar's surface increases following alternating freeze-thaw aging, acid rain aging, and alternating dry-wet and freeze-thaw aging, with increases of 0.29 %, 0.41 %, and 0.08 % respectively, while the peak intensity of C1s decreases. These observations indicate that functional groups containing carbon and oxygen elements are involved in the process of TCIPP adsorption onto aged biochar (Luo et al., 2024).

Further peak fitting (Table 5) reveals that after the adsorption of TCIPP, both original and aged biochars exhibited an increase in the proportion of C-C bonds representing the helical structure of aromatic carbon and benzene rings, as well as C-O bonds representing alcohols and phenols. Since TCIPP molecules contain π bonds, P and H atoms, this suggests that during the adsorption of TCIPP by biochar, π - π interactions, pnictogen- π interactions, and hydrogen bonding may be present (Bauzá et al., 2012; Wang et al., 2020b). It is noteworthy that the magnitude of increase in the proportion of C-C/C-O bonds on the surface of biochar aged by different methods varies, which may indicate differing intensities of π - π interactions, pnictogen- π interactions, and hydrogen bonding. Both $\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{O}$ functional groups exhibit high reactivity, providing sites for the chemical adsorption of organic pollutants onto biochar (Tan et al., 2020). In this study, after the adsorption of TCIPP by both original and aged biochar, the proportions of $\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{O}$ bonds increased, indicating the presence of chemical adsorption during the process of TCIPP adsorption by biochar. In particular, the significant increase in the proportion of $\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{O}$ bonds on the surface of biochar aged by microbial and alternating dry-wet and freeze-thaw after adsorbed TCIPP indicates that chemical adsorption plays a crucial role in the adsorption of TCIPP by these two types of aged biochar. This is consistent with the results obtained from isothermal adsorption experiments. After adsorbing TCIPP, there is a slight decrease in the proportion of O-H and C-OOH functional groups on the surface of biochar, which also indicates the presence of chemical adsorption during the process of biochar adsorbing TCIPP.

4. Conclusions

Aging can significantly alter the surface morphology and physico-chemical characteristics of biochar. Following aging, the polarity of biochar is notably enhanced, while both the aromaticity and hydrophobicity are notably weakened. Additionally, the carbon content decreases significantly, while the oxygen content increases significantly, resulting in a decrease in pH value, specific surface area, and crystallinity. Among these effects, acid rain aging has the greatest impact on the surface morphology, elemental content, and crystallinity of biochar, whereas alternating dry-wet and freeze-thaw aging has the most pronounced influence on the specific surface area of biochar. The total amount of acidic oxygen-containing functional groups on the biochar's surface increases significantly by 0.14 mmol/g (CS700-D), 0.62 mmol/g (CS700-A), 0.10 mmol/g (CS700-F), 0.22 mmol/g (CS700-M), and 0.17 mmol/g (CS700-DF), respectively. Aging also significantly alters the capacity and mechanism of biochar in adsorbing TCIPP. Specifically, after alternating dry-wet aging, microbial aging, alternating freeze-thaw aging, and alternating dry-wet and freeze-thaw aging, the highest amount of TCIPP that biochar can adsorb increased by 51.73 %, 80.59 %, 53.89 %, and 15.11 %, respectively. However, after acid rain aging, the highest amount of TCIPP that biochar can adsorb decreased by 53.37 %. The adsorption of TCIPP by biochar involves various interactions such as pore filling, hydrophobicity, hydrogen bonding, van der Waals forces, π - π interactions, pnictogen- π interactions, and more. The impact of aging on the adsorption of TCIPP by biochar is mainly reflected in the intensity of the interactions, with relatively minor changes in the types of interactions involved. In brief, after treatment with naturally gentle aging methods (excluding acid rain aging), the capacity of biochar on TCIPP adsorption was significantly enhanced. This suggests that natural aging does not cause the reactivation of TCIPP which is adsorbed and immobilized by biochar, indicating great potential regarding the use of biochar to remediate TCIPP contamination in soil.

CRedit authorship contribution statement

Luo Qing: Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Dai Wenju:** Formal analysis. **He Qing:** Formal analysis. **Deng Yongyao:** Investigation. **Li Yujie:** Investigation, Formal analysis. **Zhao Xinye:** Visualization, Investigation.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.eti.2025.104053](https://doi.org/10.1016/j.eti.2025.104053).

Data availability

Data will be made available on request.

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