

Research article

Adsorption, immobilization mechanisms and potential risks of Cd in soil-biochar-microplastics system



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ABSTRACT

The problem of cadmium (Cd) and microplastic compound contamination in agricultural soils is becoming more and more prominent. However, research on biochar remediation for heavy metal-contaminated soils often overlooks the impact of microplastics. This investigation explored Cd adsorption and immobilization of biochar in soils containing varying percentages (0 %, 2 %, 4 %, 6 %, 8 %, and 10 %) of 500-mesh polyethylene microplastics (MP500). Additionally, it examined the quantitative Cd adsorption mechanisms of biochar in the soil. The findings revealed that the Cd adsorption capacity of biochar continuously increased 1.5 %–33.1 % as the percentage of MP500 in the soil rose from 0 % to 10 %. However, higher MP500 concentrations also led to greater Cd leaching into the environment (continuously increased, 17.5 %–58.6 %) and a reduction in the proportion of relatively stable Cd (continuously decreased, 7.9 %–15.4 %) in soil-biochar samples. This suggested that microplastics interfered with biochar's effectiveness in remediating Cd contamination in soils. For adsorption mechanisms, the larger the percentage of MP500 in the soil, the greater the percentage of mineral mechanism of biochar. This study highlighted that Cd adsorbed on microplastics was a greater threat to the agricultural soil environment compared to Cd in soils; microplastics should be paid special attention to as an influencing factor in the practical application of biochar for the management of Cd pollution.

1. Introduction

Heavy metal contamination is a highly publicized pollutant affecting the sustainable utilization of agricultural soils, threatening food security and human health (Ali et al., 2023; Rai et al., 2019; Xu et al., 2023). Cadmium (Cd) is widely regarded as one of the most toxic and mobile heavy metals, prompting the development of numerous techniques to address Cd contamination in soils (Rizwan et al., 2016, 2018; Wang et al., 2025). Biochar, a material produced by pyrolyzing industrial and agricultural waste, serves as an effective in-situ passivator that can immobilize heavy metals in soils. It not only adsorbs Cd in the soil but also enhances soil properties (pH, cation content, mineral composition), thereby improving the immobilization of Cd in the soil (Duan et al., 2023; Gueret Yadiberet Menzembere et al., 2023; Lehmann et al., 2011). However, the actual field environment is more complex. Studies have shown that microplastics are widespread in agricultural soils due to the residual agricultural plastic film, the use of organic fertilizers, and

agricultural irrigation; moreover, microplastic concentrations in agricultural soil will continue to increase in the coming decades (Lan et al., 2024; Nizzetto et al., 2016; Zhang et al., 2020). The problem of Cd and microplastic compound contamination in agricultural soils is becoming more and more prominent, and some studies have shown that the Cd content in agricultural soils is significantly correlated with microplastic abundance (Liao et al., 2023; Zhou et al., 2019). The intervention of microplastics affects the environmental behavior of Cd at the soil-biochar interface, which in turn changes Cd adsorption and immobilization effect of biochars (Bi et al., 2024; Zhang et al., 2024). Therefore, understanding the biochar remediation for Cd pollution in soils with microplastic coexistence is crucial.

Currently, numerous investigations explored adsorption behaviors of heavy metal ions by biochars or microplastics individually in solutions (Bradney et al., 2019; Feng et al., 2022; Wang et al., 2022). The findings consistently showed that biochar's adsorption capacity (38.6–121.8 mg kg⁻¹) far exceeded that of microplastics (PE, PP, PS, PBT, etc.,

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$0.16\text{--}12.24 \text{ mg kg}^{-1}$) at the same Cd(II) concentration, because biochar was significantly better than microplastics in terms of mineral composition, specific surface area, and surface functional groups (Liu et al., 2024; Meng et al., 2024b; Zhang et al., 2024). Meng et al. (2024b) investigated the adsorption behaviors of Cd(II) on biochar under coexistence with polyethylene microplastics in aqueous solutions, indicating that microplastics could act both as “Cd(II) carriers” and as “pollutants adsorbed by biochar”. For soils, current research indicated that biochar could effectively immobilize Cd in soils, while microplastics posed a risk of activating Cd in soils (An et al., 2023; Gao et al., 2020). However, there are few studies on how microplastics affect the Cd adsorption and immobilization of biochar in agricultural soil. Microplastics can both adsorb Cd and occupy soil adsorption sites; therefore, in the “Soil-Biochar-Microplastics” system, it is needed to investigate how microplastics affect the transport of Cd between soil and biochar; and whether microplastics have positive or negative effects on the immobilization of Cd on the biochar and soil. In addition, the percentages of microplastics present in the soil can also influence biochar’s ability to adsorb and immobilize Cd. Therefore, understanding how Cd transports and passivates between soil and biochar in environments with varying levels of microplastics is essential for developing effective remediation strategies.

In addition to remediation behaviors, microplastic coexistence also affects Cd adsorption and immobilization mechanisms in soils by biochar. Soil immobilization mechanisms for Cd mainly include ion exchange and chemical adsorption by soil organic matter (Cao et al., 2024; Li et al., 2023b). Microplastics in soil occupy Cd adsorption sites, which in turn can alter Cd immobilization mechanisms by soil. Cd adsorption mechanisms by biochar from soils mainly include functional group complexation, ion exchange and mineral precipitation (Deng et al., 2019; Gao et al., 2020; Meng et al., 2024a). The microplastics in soils can also adsorb Cd through electrostatic attraction, hydrogen bonding binding, and functional group complexation, which may impact the adsorption mechanisms for Cd by biochar from the soil (Meng et al., 2024b; Zhang et al., 2020). Coexistence of microplastics may alter the Cd adsorption and immobilization mechanisms of biochar, which in turn poses challenges for biochar remediation of soil Cd pollution. This makes it critical to study how microplastics influence Cd adsorption mechanisms by biochar within “Soil-Biochar-Microplastics” system.

In this study, Cd-contaminated soils containing different proportions of microplastics were subjected to a 180-day co-ageing process with biochar (Acidified and unacidified). The employment of the three-layer mesh method not only ensured close contact between the soil and biochar during the ageing process, but also facilitated the easy separation of the soil and biochar after ageing. Thereby, the kinetic adsorption behaviors in soils with different proportions of microplastics and the quantitative adsorption mechanism of biochar within the “Soil-Biochar-Microplastics” system were investigated. We aimed to test the hypothesis that the microplastics would affect Cd adsorption and immobilization mechanisms in soils by biochar, and the effects vary with the percentages of microplastics. The main objectives were 1) to examine how microplastics impact the adsorption and immobilization of Cd in soils by biochar; 2) to compare how varying proportions of microplastics in soils affect biochar’s ability to remediate Cd contamination; 3) to uncover shifts in the quantitative mechanism of Cd adsorption by biochar in soils with different microplastic percentages.

2. Materials and methods

2.1. Preparation of Cd-microplastics complex contaminated soils

The soil sample employed in this experiment was an acidic soil ($\text{pH} = 5.16$, Clayic Dystric Alisols), which was collected from a paddy field in Nanchang City, Jiangxi Province. Soil samples from the 0–10 cm layer were taken, large stones were sorted out, and the soil samples were dried, ground, and sieved in the laboratory for use. The soil texture is clay loam, and the organic matter and CEC of the soil are 4.42 g kg^{-1} and

$9.53 \text{ cmol}(+) \cdot \text{kg}^{-1}$, respectively. According to Fuller and Gautam (2016), the microplastic contents in soil was up to 6.7 %. With the continuous development and application of plastic products, the proportion of microplastics in farmland soil will further increase. Therefore, to explore how varying levels of microplastics affect biochar’s ability to remediate Cd contamination in agricultural soils, 6 gradient significant proportions of microplastics addition were selected in this study, which were 0 %, 2 %, 4 %, 6 %, 8 %, and 10 %, respectively. Polyethylene is one of the most frequently used plastic products in China, commonly used as agricultural landfilm, and was applied in this experiment. Polyethylene pellets were purchased from Cheng Cheng Plasticizing Co. Ltd. in Dongguan, China, with a particle size of 500 mesh (MP500, 30 μm). The C and H contents of MP500 are 85.49 % and 14.04 %, and the specific surface area, charge and density of MP500 are $1.98 \text{ m}^2 \text{ g}^{-1}$, -37.7 mV, and 0.945 g cm^{-3} . Firstly, different amounts of MP500 were added to the sieved soil to prepare soils with 2 %, 4 %, 6 %, 8 %, and 10 % of MP500. For example, when configuring soil containing 4 % MP500, 40 g of MP500 was added to 960 g of soil. Secondly, an equal volume of $\text{Cd}(\text{NO}_3)_2$ solution was added to soils (not contaminated with Cd) with varying proportions of MP500, ensuring that all samples reached a consistent Cd concentration of 10 mg kg^{-1} . 1 kg of soil was first added to 1 L of a 10 mg L^{-1} $\text{Cd}(\text{NO}_3)_2$ solution, then ultra-pure water was added to submerge the soil sample. The soil-water mixture was thoroughly stirred with a glass rod, and the soil sample was cultured at 25°C . Finally, after equilibrating the soil samples for a month, they were ground as well as sieved for the next step.

2.2. Preparation of biochars

Biochar was produced from rice straw, a common agricultural waste, and the application of rice straw biochar can not only remediate Cd pollution, but also achieve waste utilization. Previous research demonstrated that KMnO_4 -modified biochar significantly enhanced Cd adsorption and immobilization compared to unmodified biochar; therefore, this study also utilized KMnO_4 -modified rice straw biochar (MBC). The sieved straw powder (less than 0.3 mm) was fully mixed with a 0.1 mol L^{-1} KMnO_4 solution using a liquid-to-solid ratio of 1:5; the mixture was sonicated for 2 h and then dried, crushed, and placed into a crucible, kept at 400°C for 4 h in a muffle furnace (Meng et al., 2022). The C, H, N, O contents of MBC are 48.42 %, 2.36 %, 1.00 %, and 25.98 %, and the specific surface area, pH and pH_{pzc} of MBC are $19.40 \text{ m}^2 \text{ g}^{-1}$, 9.60 and 1.98. To analyze the contributions of Cd adsorption mechanisms, acidified biochar (AMBC) was also prepared. MBC was treated with a 1 M HCl solution, shaken for 24 h, filtered, and rinsed with ultrapure water until the filtrate’s pH stabilized. After oven drying, the AMBC was ready for use.

2.3. Co-ageing process of biochars and Cd-MP500 complex contaminated soils

In this study, to explore the Cd adsorption behaviors and mechanisms by biochar in soils with varying proportions of MP500, a three-layer mesh method developed in previous research (Meng et al., 2020) was employed. Each three-layer mesh setup included 100 g of contaminated soil and 3 g of biochar (a 3 % biochar application ratio). The layers ($15 \text{ cm} \times 20 \text{ cm}$) were arranged sequentially: 50 g of soil in the upper layer (2 mm), 3 g of biochar in the middle layer (1 mm), and 50 g of soil in the lower layer (2 mm). The sufficient thinness of each layer ensured that substances and Cd were conducted and exchanged through water, maximizing the similarity of the three-layer mesh method to actual field conditions. Each layer was separated by 600-mesh nylon mesh (less than 0.1 mm) to facilitate separation after co-ageing, and the bottom and top were secured by perforated stainless steel plates and clips. This design maximized the contact area between the soil and biochar, enhancing interaction for effective analysis. There were 6 types of contaminated soils, namely Cd contaminated soils with MP500

percentages of 0 %, 2 %, 4 %, 6 %, 8 %, and 10 %; and 2 types of biochar, namely MBC and AMBC.

To study the kinetic adsorption process of Cd by biochar in contaminated soil, this research utilized a constant temperature and humidity ageing method with a constant temperature humidity chamber (Boxun Company, China). The temperature is always maintained at 25 °C, and moisture was maintained at 80 % weight moisture content, and three-layer mesh samples were weighed and rehydrated every other day. The amount of water needed to replenish each sample varied, but the principle was to replenish it to the corresponding 80 % weight moisture content of the sample. The whole ageing process was carried out for a total of 180 days (from March 15, 2024 to September 11, 2024) and the corresponding samples were removed at day 10, 30, 60, 120 and 180, respectively. For aged three-layer mesh samples, they were first thoroughly dried, and subsequently disassembled and sampled. The soil from the upper and lower layers was thoroughly mixed as the soil samples for testing, while the biochar from the middle layer was collected as the biochar sample for analysis. This treatment not only simulated the 3 % biochar application ratio in actual fields, but also avoided the effects of differences in properties between the aged upper and lower layers of soil.

2.4. Characterization and Cd analysis of biochar and soil samples

To analyze how the physicochemical properties of biochar changed after co-ageing with soil, measurements were taken for pH, functional groups, mineral crystals, elemental composition, and morphological characteristics of both fresh and aged biochar samples. The surface morphology of biochar samples was analyzed using field emission scanning electron microscopy-energy dispersive spectroscopy. Moreover, the changes in functional groups and mineral crystals on biochar samples after the aging process were identified by Fourier transform infrared spectroscopy and X-ray diffraction. The specific instruments used for these analyses are detailed in the Supplementary Materials (Table S1). Additionally, to assess the impact of microplastic content on soil properties, the specific surface area of soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500 was also measured.

To analyze Cd concentrations, soil and biochar samples were first digested using a microwave digestor. Soil samples were treated with the HNO₃-HF-HCl method, while biochar samples were processed using the HNO₃-HClO₄-HCl method (USEPA, 1996). The Cd adsorption levels in biochar and the Cd concentrations in the soil after co-ageing were measured using flame atomic absorption spectrometry (AAS, USA). The adsorption of Cd by biochar at various ageing time points was then used to fit adsorption kinetic curves. Subsequently, the Tessier sequential extraction method (Table S2, Supplementary Materials) was conducted to classify the remained Cd in the soil into 5 fractions, where exchangeable Cd (F1) is the most active and threatening fraction to the soil environment, crops, and humans, and the residual Cd (F5) is the most stable fraction and can only be utilized in extreme cases (Feng et al., 2024; Pan et al., 2023; Tessier, 1979). In addition, the F1 concentration of Cd on biochar was also determined, but F2-F5 were not determined because the straw biochar powder was too dense to be separated by centrifugation. The amount of Cd leached into the environment during the ageing process was calculated by subtracting the Cd in soils and the Cd adsorbed by the biochar from the total Cd content in the original soil.

2.5. Quality control and statistical analysis

In this investigation, experimental data were averaged from triplicate measurements, with error bars in the figures representing the variability among the three results. Data analysis for this experiment was performed using EXCEL 2019, while data fitting and graph plotting were carried out with Origin 2018. The kinetic curves for Cd adsorption by biochar from contaminated soils over 180 days of ageing were fitted

using both the pseudo-first-order (PFO) and pseudo-second-order (PSO) adsorption kinetic equations, as detailed in the Supplementary Materials (equations S1 and S2). Additionally, to determine the contributions of Cd adsorption mechanisms, the adsorption concentration of acidified biochar represented the non-mineral mechanism, while the difference between non-acidified and acidified biochar adsorption concentrations represented the mineral mechanism. MBC and AMBC were digested and the concentrations of K, Na, Ca, Mg, and Mn were measured by inductively coupled plasma mass spectrometry. After being treated with the HCl solution, the proportions of K, Na, Ca, Mg, and Mn on AMBC decreased by over 93 % compared with those on MBC. This indicated that mineral components on biochars were almost completely removed. These calculations were based on equations S3 and S4 in the Supplementary Materials.

3. Results and discussion

3.1. Changes in biochar and soil physicochemical properties during ageing

Changes in the physicochemical properties of biochar and soil can provide insights into biochar's effectiveness in remediating Cd contamination (Bandara et al., 2021; Kumar et al., 2018). As illustrated in Fig. 1a-f, rice straw biochar exhibited a well-developed pore structure, with a specific surface area of 19.40 m² g⁻¹ for modified biochar (MBC). The surface of fresh biochar appeared smooth and intact (Fig. 1a). However, as biochar aged alongside soil, its surface became increasingly rough and fragmented (Fig. 1b-f), leading to pore collapse and blockage, which reduced its specific surface area (Ren et al., 2018; Wang et al., 2017). The specific surface area of soil without microplastics was 21.41 m² g⁻¹, while that of microplastics (MP500) was only 1.98 m² g⁻¹. Consequently, the introduction of microplastics into the soil significantly decreased its specific surface area. In this study, the specific surface area of soils containing 2 %, 4 %, 6 %, 8 %, and 10 % MP500 was 20.43, 19.71, 17.67, 16.84 and 16.42 m² g⁻¹, respectively (Table 1). The decrease in the specific surface area of the soil would weaken its ability to immobilize Cd, which thereby led to the leaching loss into the environment or the adsorption by biochar. Fig. 1g displays the changes in pH values of biochars and soils during ageing at the MP500 percentage of 10 %. During 180-day ageing, the pH of the soil continued to increase while that of the biochar gradually declined due to the difference in initial pH between the soil and the biochar, which were stabilized at the late stages of ageing. The pH of both biochar and soil changed the most during the first 10 days of ageing, indicating that the transport of substances on both was most intense at the beginning of ageing and slowed down with ageing time. Moreover, as shown in Table 1, the higher the percentage of microplastics in the soil, the greater the pH of the aged soil and biochar. When biochar was applied to the soil, it used its inherent alkalinity to enhance the soil's pH. As the microplastic contents in soil increased, the proportion of real soil decreased, and the proportion of soil requiring pH improvement decreased accordingly. As a result, each unit of biochar had a more pronounced effect on raising the soil's pH, while the biochar itself experienced less consumption, ultimately leading to an overall increase in the sample's pH.

For the variation of elemental contents on biochar, the most representative are the O content, Si content and the total amount of metal cations (Fig. 1h). As ageing proceeded, the O content on the biochar gradually increased, indicating that the biochar was oxidized during ageing. In turn, the oxidation of biochar resulted in alterations to the oxygen-containing functional groups on its surface (Cui et al., 2021; Liu et al., 2020). As shown in Fig. 1i, the main types of functional groups on biochar included C-H, C=O, C-O, -OH, and C-H₂, of which C-O and C-H₂ on aged biochars underwent some degree of blueshift (Chen et al., 2024b; He et al., 2019). The Si content as well as the total amount of metal cations on the biochar and XRD images (Fig. 1j) correspond to each other. For fresh biochar, the primary mineral crystals were KCl and

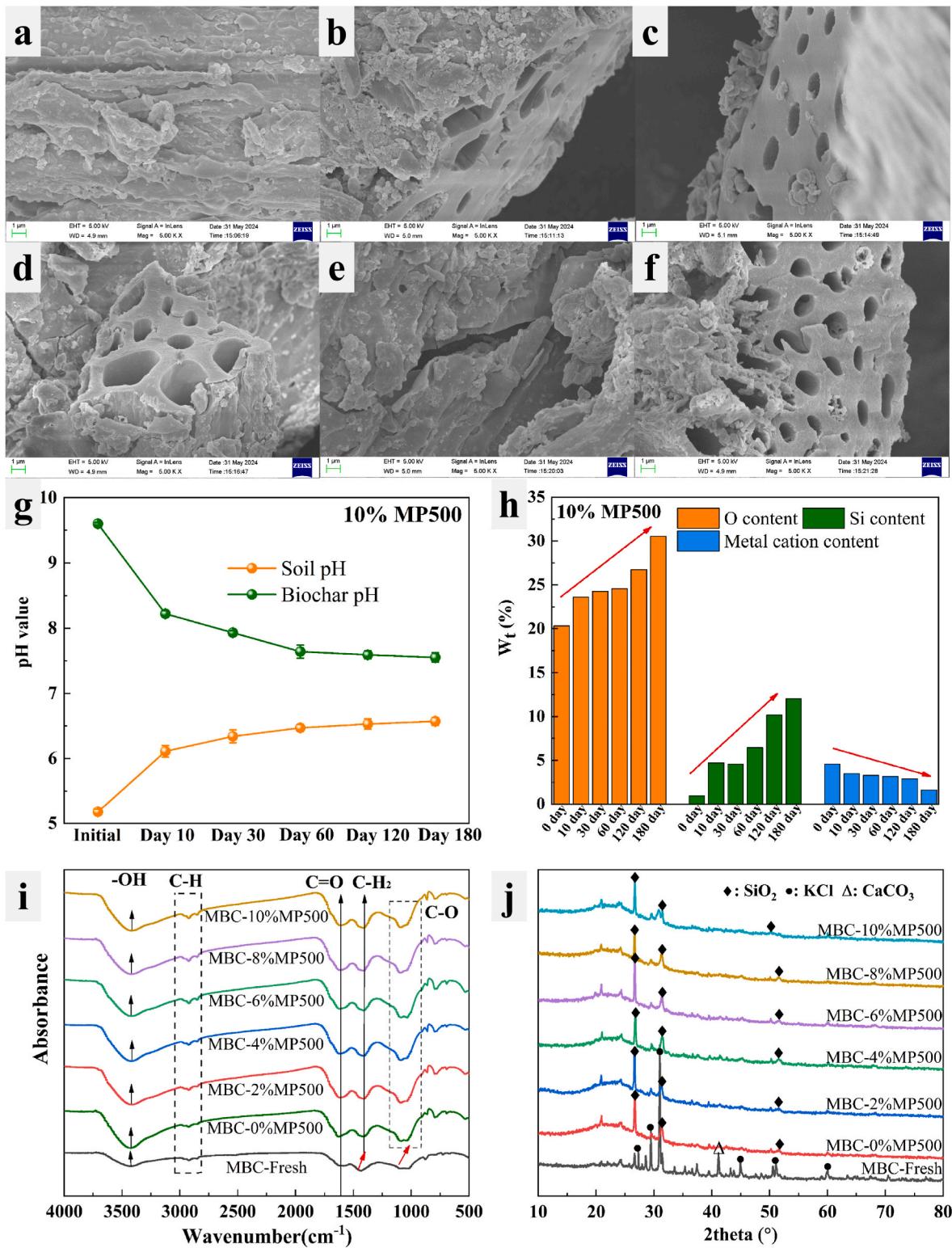


Fig. 1. Characteristic changes in MBC after the co-ageing process in soils containing MP500: SEM images of MBC with ageing time (a–f); pH changes in MBC and soil (g); changes in O, metal cation, and Si contents of MBC (h); FTIR (i) and XRD (j) analysis of MBC before and after ageing.

Notes: MBC is KMnO₄-modified rice straw biochar; MP500 is 500-mesh polyethylene microplastics; MBC-Fresh is initial biochar; MBC-0 %MP500, MBC-2 %MP500, MBC-4 %MP500, MBC-6 %MP500, MBC-8 %MP500, MBC-10 %MP500 are biochars aged with the soil containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500.

CaCO₃. However, after co-ageing with soil, the main mineral crystals shifted to SiO₂. This transformation led to a significant increase in the percentage of Si on the biochar. Additionally, during the co-ageing process, the loss of K, Na, Ca, Mg, and Mn from the biochar, either to the soil or through ion exchange with Cd in the soil, resulted in a notable

reduction in the total metal cation content. This was also evident from the disappearance of CaCO₃ in XRD images (Fig. 1j). The significant decrease in metal cations on the biochar suggested two key outcomes: firstly, Cd from the soil was transported to the biochar, and secondly, biochar's adsorption and immobilization capacity gradually declined

Table 1

The basic properties of soil, biochar, and microplastics.

Soil	pH	Texture	Sand (%)	Silt (%)	Clay (%)	Organic matter ($\text{g}\cdot\text{kg}^{-1}$)	CEC ($\text{cmol}(\text{+})\cdot\text{kg}^{-1}$)
Biochar	5.18 ± 0.04	Loamy clay	45.0	20.0	35.0	4.42	9.53
	pH	C (%)	H (%)	N (%)	O (%)	BET-SA ($\text{m}^2\cdot\text{g}^{-1}$)	pH_{pzc}
	9.6 ± 0.02	48.42	2.36	1.00	25.98	19.40	1.98
Microplastics	C (%)	H (%)	N (%)	O (%)		BET-SA ($\text{m}^2\cdot\text{g}^{-1}$)	
	85.49	14.04	0.00	0.00		1.98	
Soil-180 days (containing MP500)	0 %MP500	2 %MP500	4 %MP500	6 %MP500	8 %MP500		10 %MP500
pH	6.20	6.27	6.29	6.38	6.52		6.57
Biochar-180days (containing MP500)	0 %MP500	2 %MP500	4 %MP500	6 %MP500	8 %MP500		10 %MP500
pH	7.12	7.20	7.25	7.38	7.44		7.55
Soil (containing MP500)	0 %MP500	2 %MP500	4 %MP500	6 %MP500	8 %MP500		10 %MP500
BET-SA ($\text{m}^2\cdot\text{g}^{-1}$)	21.41	20.43	19.71	17.67	16.84		16.42

over the ageing process (Li et al., 2024; Meng et al., 2024a).

3.2. Adsorption kinetics of Cd by biochar in soils containing MP500

Similar to its behavior in aqueous solutions, Cd adsorption of biochar in soils followed a time-dependent pattern (Chen et al., 2024a; Deng et al., 2020). Previous studies have rarely explored biochar's adsorption behaviors in soil due to the challenge of separating biochar from the soil after co-ageing. However, it's important to note that biochar's adsorption of Cd in soils plays a critical role in remediating Cd contamination (Li et al., 2023a; Wang et al., 2023). In this study, the dynamic 180-day adsorption process of Cd in soils containing MP500 by biochar was examined, and the adsorption data were fitted using PFO and PSO kinetic models. The fitted curves are shown in Fig. 2a. Regardless of the MP500 proportion, the Cd adsorption curves in soils by biochar exhibited an inverted "L" shape. Specifically, Cd adsorption was most intense during the early stages of ageing, particularly within the first 30 days. After 30 days, the total amount of Cd adsorbed by biochar stabilized, with only slight increases observed over time.

The adsorption coefficients derived from the PFO and PSO kinetic models are presented in Table 2. Compared to the PSO model, the PFO model yielded higher R^2 values. As shown in Fig. 2b and Table 2, the adsorption of Cd by biochar increased significantly with higher percentages of MP500 in the soil. The Q_1 values for biochar adsorption in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500, as fitted by the PFO kinetic model, were 100.94, 104.18, 113.13, 124.98, 129.70, and 131.73 $\text{mg}\cdot\text{kg}^{-1}$, respectively. This phenomenon could be attributed

to two main factors. Firstly, the adsorption capacity of microplastics in this study for Cd in aqueous solution was significantly greater than that of soil (Fig. S4 in Supplementary Materials). However, the ability of microplastics to immobilize Cd was significantly weaker than that of soil (Section 3.4), which led to the fact that biochar could adsorb Cd from microplastics more easily. Therefore, biochar adsorbed more Cd from microplastic coexisting soils compared to single soils. Moreover, due to the factors such as the specific surface area of MP500 being significantly smaller than soil, it was significantly easier for biochar to adsorb Cd from MP500 than from soil. Secondly, in the presence of microplastics, the pH values of both aged biochar and soil increased compared to when microplastics were absent, which also led to an increase in the adsorption capacity of biochar for Cd. Therefore, based on this, a higher proportion of MP500 in the soil enhanced the Cd adsorption by biochar.

These findings contrasted significantly with results from aqueous solutions. Meng et al. (2024b) demonstrated that microplastic particles in aqueous solutions hindered biochar's adsorption of heavy metal ions. In aqueous solutions, microplastics acted as adsorbents for heavy metal ions while also being adsorbed by biochar, occupying biochar's adsorption sites and reducing its capacity to adsorb heavy metal ions. However, the immobilization of Cd adsorbed onto microplastics was significantly weaker compared to its immobilization in soil. Microplastics mainly immobilized Cd through electrostatic adsorption and physical adsorption, while soil could also immobilize Cd through ion exchange and mineral precipitation. Cd existed in soil in the form of organic matter and sulfide compounds, or even as residues. Therefore, for Cd immobilized on microplastics, biochar had significantly lower

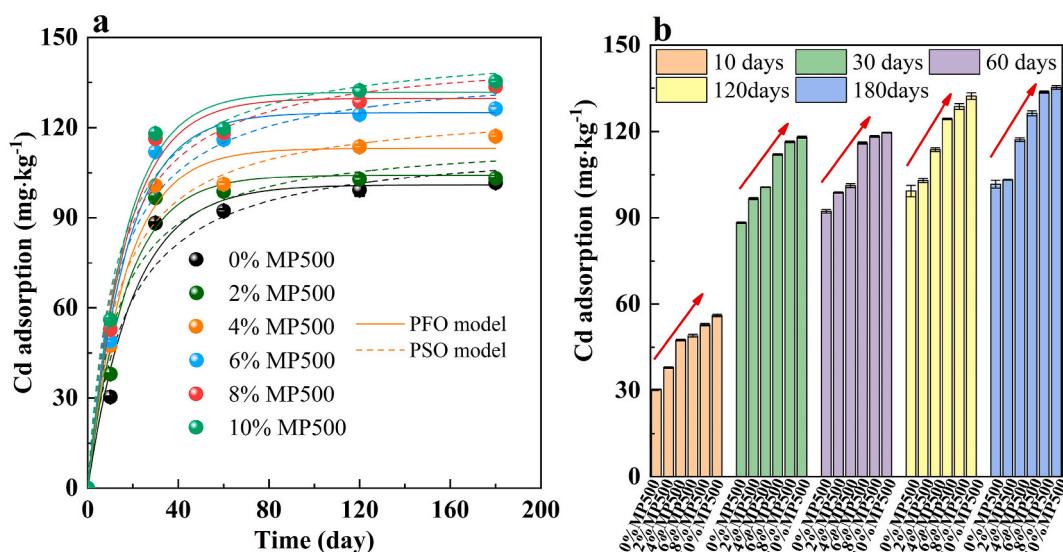


Fig. 2. The adsorption kinetics curves of Cd by MBC in soils containing MP500 fitted by pseudo-first-order and pseudo-second-order kinetic models (a); the Cd adsorption capacities of MBC in soils containing MP500 at different ageing time points (b).

Notes: PFO model is pseudo-first-order adsorption kinetic model; PSO model is pseudo-second-order adsorption kinetic model.

Table 2

Cd adsorption coefficients of MBC in soils with 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % of MP500 fitted by pseudo-first-order kinetic and pseudo-second-order kinetic models.

Biochar adsorption in soils with different ratios of MP500	Pseudo-first-order model			Pseudo-second-order model		
	Q ₁ (mg·kg ⁻¹)	K ₁ (day ⁻¹)	R ²	Q ₂ (mg·kg ⁻¹)	K ₂ (kg·mg ⁻¹ ·day ⁻¹)	R ²
0 % MP500	100.94	0.049	0.973	115.63	0.0005	0.947
2 % MP500	104.18	0.059	0.976	116.84	0.0006	0.943
4 % MP500	113.13	0.059	0.983	127.26	0.0006	0.975
6 % MP500	124.98	0.059	0.986	140.42	0.0005	0.966
8 % MP500	129.70	0.060	0.985	145.78	0.0005	0.970
10 % MP500	131.73	0.061	0.986	147.66	0.0005	0.975

difficulty in obtaining it than in adsorbing it from soil. As a result, biochar's ability to adsorb Cd from soil was more effective in the presence of microplastics than in their absence.

3.3. Changes in Cd fractions by biochar in soils containing MP500

In situ passivation techniques can not reduce the Cd concentration in soils, of which the effectiveness of biochar in remediating Cd pollution ultimately depends on the fraction distributions of Cd in the soil. The fraction distributions of Cd in soils containing different proportions of MP500 are shown in Fig. 3, moreover, the overall situation at the 10th and 180th days of ageing is also demonstrated. As ageing progressed, Cd leaching from the soil was inevitable, and the longer the ageing time, the greater the leaching loss. For all contaminated soils, the addition of biochar significantly reduced the leaching loss of Cd into the environment compared to the control (CK) treatment. For example, in the soil containing 10 % MP500, the Cd leaching loss under CK treatment was 192.5, 223, 231.5, 263.5, and 281.5 µg at the 10th, 30th, 60th, 120th, and 180th days of ageing, respectively; while that under MBC treatment was 122.5, 165.5, 186.13, 191.25, and 231.75 µg. Biochar prevented Cd leaching from soil mainly through two pathways, the first was that biochar immobilized Cd in itself through adsorption of Cd, although Cd immobilized on biochar might also have the risk of leaching, but it could ensure that the vast majority of Cd was stabilized; the second was that biochar transformed active Cd in the soil into a more stable form by enhancing the soil's physical and chemical properties, such as increasing its pH value (Fig. 1g). This process reduced the leaching of Cd within the soil (Jia et al., 2021; Zhu et al., 2024a). Similarly, Hamid et al. (2024) demonstrated that wheat straw biochar reduced the leaching of lead (Pb) and Cd by 61.00 % and 56.39 %, respectively, in contaminated soils under flow-through conditions.

With increasing ageing time, although the leaching loss of Cd from the soil rose, the adsorption of Cd by biochar simultaneously increased, leading to a significant reduction in the amount of exchangeable Cd in the soil. For instance, compared with CK, the amount of exchangeable Cd in the soil decreased by 18.09 %, 27.62 %, 43.49 %, 43.58 %, and 52.27 % at the 10th, 30th, 60th, 120th, and 180th days of ageing, respectively. The significant reduction in exchangeable Cd in soils compared to the CK treatment can be attributed to two main factors. On the one hand, biochar adsorbed a substantial amount of Cd from the soil, with a preference for exchangeable Cd. On the other hand, biochar improved soil properties, facilitating the transformation of exchangeable Cd into more stable forms (Bashir et al., 2020; El-Naggar et al., 2022).

Regarding the impact of varying MP500 percentages in soils, a higher proportion of MP500 led to greater leaching loss of Cd. This was because the actual soil fraction had a higher Cd concentration; moreover, the Cd adsorbed onto MP500 was more prone to leaching into the environment compared to Cd in the actual soil fraction. Cd leached from soil into the environment was the most active fraction of Cd, which transported from surface soil to deeper layers (e.g., into groundwater or through lateral diffusion) or contaminated surrounding environments via surface runoff. During leaching, the fraction of Cd might change from an adsorbed state (e.g., bound to organic matter or iron-manganese

oxides) to a soluble ionic state, increasing its bioavailability in the environment, especially under acidic or low-salinity conditions. Additionally, leached Cd could be absorbed by plant roots and subsequently bioaccumulate through the food chain, posing a threat to human health (Rizwan et al., 2016). By the 180th day of ageing, the Cd leaching loss under MBC treatment was 146.13, 171.63, 187.13, 193.25, 184.13, and 231.75 µg in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500, respectively. Consequently, the higher the MP500 percentage, the greater the adsorption of Cd by biochar and the lower the amount of exchangeable Cd in the soil. The amount of exchangeable Cd under MBC treatment was 352.5, 352, 316.5, 312, 297, and 262.5 µg in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500 at the 180th days of ageing, respectively. In Section 3.4, the effects of MP500 percentages on biochar remediation of soil Cd contamination were evaluated more systematically.

3.4. Overall remediation of Cd pollution by biochar in soils containing MP500

To comprehensively assess the effectiveness of biochar in remediating Cd contamination in soils containing MP500, after ageing, in addition to the Cd leaching to the environment (Leaching loss, most negative), the Cd in the soil and biochar was divided into 3 parts: exchangeable Cd in the soil (Soil-F1, relatively negative), exchangeable Cd in the biochar (Biochar-F1, relatively negative), and relatively stable Cd in the soil and biochar (Relatively stable fraction, most positive). For the overall soil-biochar sample, the lower the percentage of Cd leaching loss and the higher the proportion of relatively stable Cd, the more effective biochar is at remediating Cd contamination. As shown in Fig. 5, at the end of aging, for CK treatments (no biochar treatment, only soil and microplastics), the higher the percentage of microplastics, the greater the leaching loss of Cd to the environment and the lower the percentage of relatively stable Cd. This indicated that the greater the percentage of microplastics in the soil, the more unstable the adsorbed Cd was and the more likely it was to transport. This also indicated that the stability of Cd adsorbed on microplastics was significantly weaker than that adsorbed on soil. In soils with varying percentages of MP500, the proportion of relatively stable Cd increased significantly under MBC treatment compared to the CK treatment. As ageing progressed, the relatively stable Cd in the CK treatment gradually decreased due to increasing soil Cd leaching loss. However, the application of MBC effectively immobilized Cd. For instance, in soil containing 10 % MP500, the percentage of relatively stable Cd under CK treatment was 19.85 %, 19.29 %, 18.83 %, 17.11 %, and 15.58 % on the 10th, 30th, 60th, 120th, and 180th days of ageing, respectively. After applying MBC, the percentages of relatively stable Cd increased by 7.38 %, 6.43 %, 4.94 %, 5.29 %, and 6.36 %. As shown in Fig. 4, biochar application significantly reduced the percentages of Cd leaching and exchangeable Cd in soils. Although some of Cd on biochar remained in the exchangeable fraction, the overall proportion of relatively stable Cd in the sample increased substantially.

As the proportion of MP500 in the soil rose, the percentages of Cd leaching loss from the samples increased, while the proportion of relatively stable Cd decreased, suggesting that the presence of microplastics

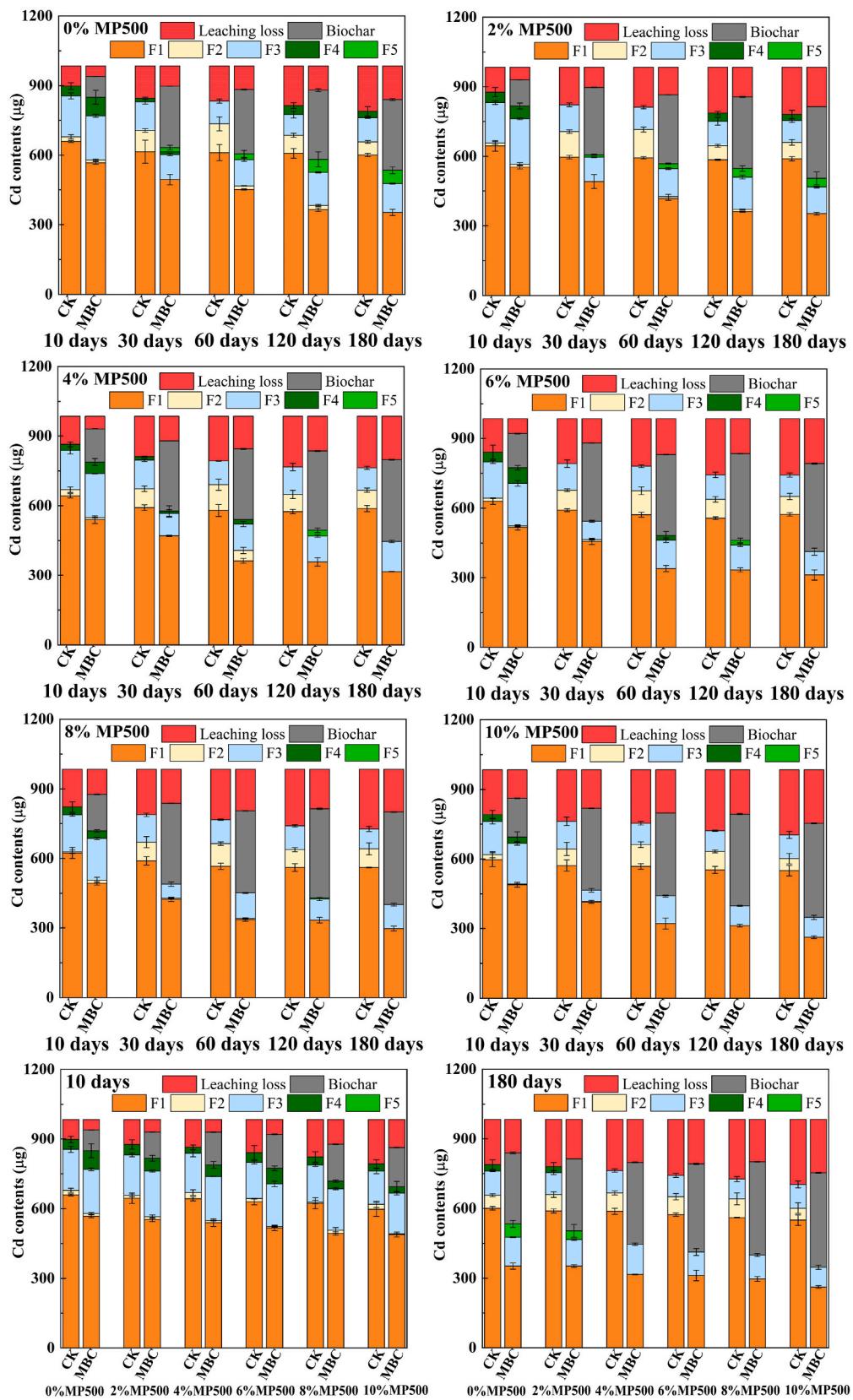


Fig. 3. Cd leaching loss, Cd adsorption by biochar, and Cd fraction distributions of soils during ageing in soils (treatments: 0 % MP500, 2 %MP500, 4 %MP500, 6 % MP500, 8 %MP500, 10 %MP500, 10 days, and 180 days).

Notes: F1, F2, F3, F4, and F5 are five fractions of Cd divided by Tessier sequential extraction method, including exchangeable fraction (F1), carbonate fraction (F2), Fe-Mn oxide-bound fraction (F3), organic fraction (F4) and residual fraction (F5). MP500 is 500-mesh polyethylene microplastics.

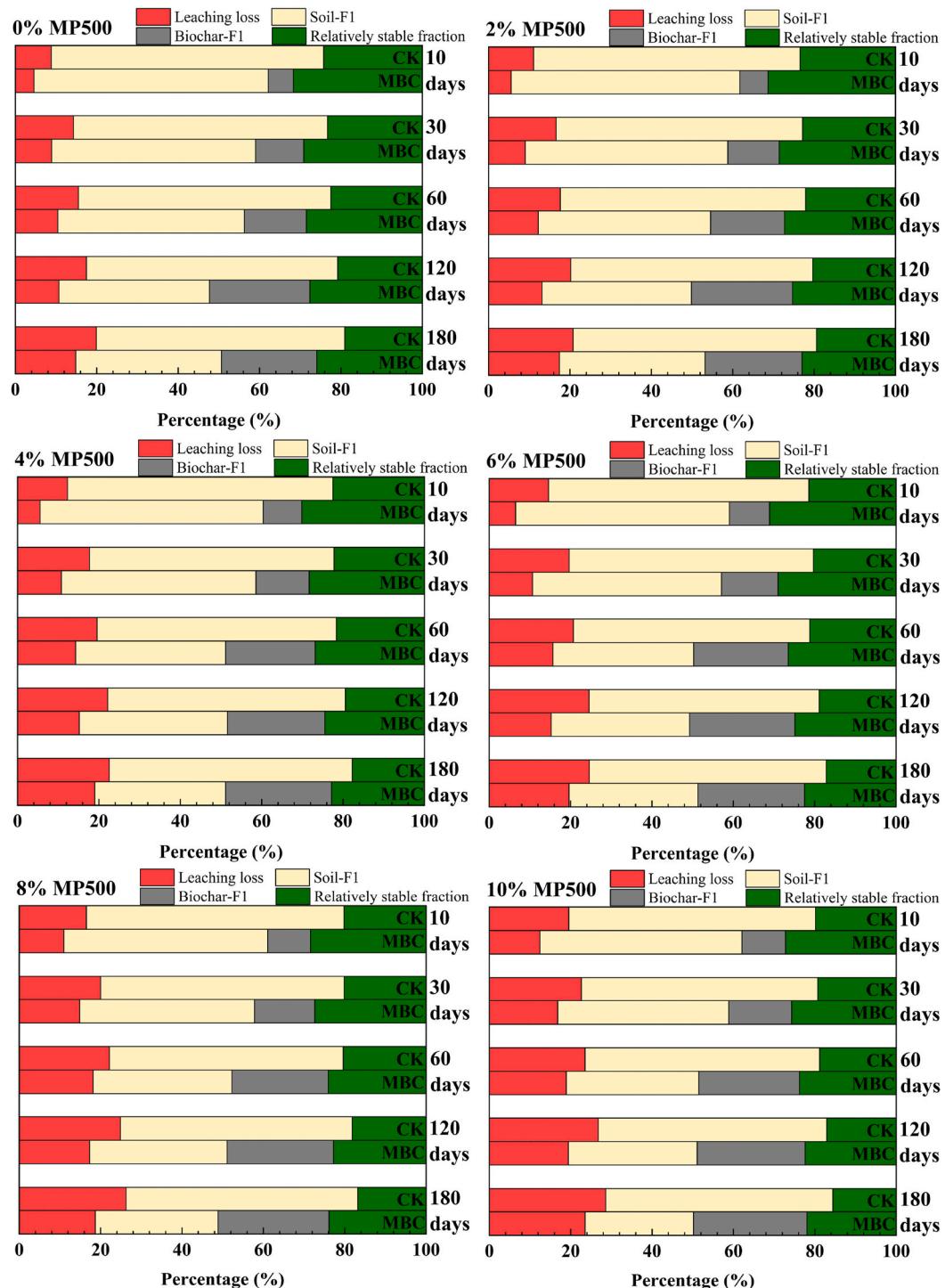


Fig. 4. Overall remediation of Cd contamination in soils containing MP500 by biochar during ageing, and the Cd in samples was divided into four fractions (Cd leaching loss, soil F1, biochar F1, and relatively stable Cd). Treatments: 0 % MP500, 2 %MP500, 4 %MP500, 6 %MP500, 8 %MP500, 10 %MP500.

Notes: MP500 is 500-mesh polyethylene microplastics; MBC is KMnO₄-modified rice straw biochar; Soil-F1 is the exchangeable Cd in the soil; Biochar-F1 is the exchangeable Cd in the biochar.

hindered the remediation of Cd contamination in soil by biochar. For instance, at the 180th days of ageing, the percentages of relatively stable Cd under MBC treatment was 25.94 %, 22.98 %, 22.84 %, 22.51 %, 23.87 %, and 21.95 % in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500, respectively (Fig. 5). Although MP500 in the soil favored the Cd adsorption by biochar, it also exacerbated the leaching of Cd from the soil to the environment. Additionally, as the percentage of microplastics increased, the rise in soil Cd leaching was significantly greater than the

reduction in soil exchangeable Cd, ultimately leading to a notable decrease in the proportion of relatively stable Cd in the samples. As summarized in Table 3, the fate of heavy metals in biochar-soil systems and microplastics-soil systems was compared. In biochar-soil systems, biochar application generally enhanced the immobilization of heavy metals (Kang et al., 2024; Lin et al., 2023; Song et al., 2022; Zhu et al., 2024b). However, in microplastics-soil systems, while Tang et al. (2024) suggested that microplastics could facilitate heavy metal passivation,

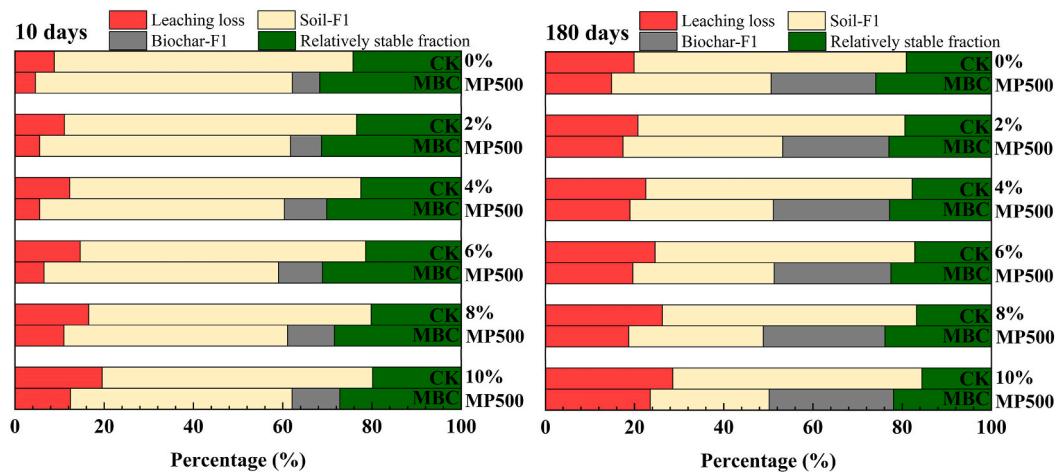


Fig. 5. Overall remediation of Cd contamination in soils containing MP500 by biochar during ageing, and the Cd in samples was divided into four fractions (Cd leaching loss, soil F1, biochar F1, and relatively stable Cd). Treatments: ageing times of 10 days and 180days.

Notes: MP500 is 500-mesh polyethylene microplastics; MBC is KMnO₄-modified rice straw biochar; Soil-F1 is the exchangeable Cd in the soil; Biochar-F1 is the exchangeable Cd in the biochar.

Table 3

The fate of heavy metals in biochar-soil systems and microplastics-soil systems.

The fate of heavy metals in biochar-soil systems	Soil	Biochar	Ageing process	Fate of heavy metals	References
	Cd and Pb contaminated soil	Amino acid-modified corn stalk biochar	Constant temperature and humidity light ageing	Biochar was effectively stabilize the heavy metals in contaminated soil and inhibited the accumulation of Cd and Pb in wheat	Zhu et al. (2024b)
	Cd and Zn contaminated soil	KMnO ₄ -hematite modified biochar	Planting experiments - natural ageing	Biochar effectively reduced the phytotoxicity of soil Cd and Zn by converting acid-soluble Cd and Zn into residual fractions	Kang et al. (2024)
	Cu, Zn, As, Cd, and Pb contaminated soil	biochar-supported nanoscale zero-valent iron	Constant temperature and humidity ageing	The residual component of Cu, Zn, As, Cd, and Pb increased by 10.27 %, 7.18 %, 7.44 %, 9.26 %, and 12.75 %, respectively.	Song et al. (2022)
	Cu and Cd contaminated soil	Mn/Al-layered double oxide-loaded biochar	Constant temperature and humidity ageing	Biochar had excellent immobilization for Cu and Cd in contaminated soil	Lin et al. (2023)
The fate of heavy metals in microplastics-soil systems	Soil	Microplastics	Ageing process	Fate of heavy metals	References
	Cr, Cd, Cu, and Zn contaminated soil	PET microplastics	Constant temperature and humidity ageing	Addition of PET microplastics increased the pH of the soils and promoted the immobilization of heavy metals	Tang et al. (2024)
	Pb, Zn, and Cd contaminated soil	Multiple microplastics	Planting experiments - natural ageing	Microplastics amplified the bioavailability of soil heavy metals, thereby increasing the accumulation of heavy metals in plant	Chebbi et al. (2024)
	Hg contaminated soil	PVC microplastics	Room temperature incubation in the dark	PVC microplastics increased the bioavailability of Hg ²⁺ in soil	Yang et al. (2022)
	Cu and Pb contaminated soil	PE microplastics	Planting experiments - natural ageing	Microplastics in the soil exacerbated the threat of heavy metals in the soil and in crops	Jia et al. (2022)

most studies found that microplastics increased the threat posed by heavy metals in soils (Chebbi et al., 2024; Jia et al., 2022; Yang et al., 2022). An et al. (2023) conducted a meta-analysis on the impact of microplastics on heavy metals in soils, concluding that polyethylene microplastics might increase the bioavailability of Cd. The findings of this study demonstrated that polyethylene microplastics exacerbated Cd leaching and hindered the remediation of Cd-contaminated soils, even when biochar was applied. Zhao et al. (2025) also indicated that compared with single biochar treatment, the DTPA-Cd content in the root zone soil significantly increased when biochar was co-treated with PLA microplastics.

3.5. Cd adsorption mechanisms of biochar in soils containing MP500

Quantifying the adsorption mechanisms of biochar helps clarify the contributions of its mineral and non-mineral components to Cd adsorption, enabling tailored solutions for different pollution scenarios. Quantify the contribution percentages of mineral mechanisms and non-mineral mechanisms to the adsorption of Cd in soils by biochar, thereby elucidating the roles of mineral mechanisms (ion exchange, mineral

precipitation) and non-mineral mechanisms (functional group complexation, other potential mechanisms). As shown in Fig. 6, the contribution of the mineral mechanism to Cd adsorption increased significantly with ageing time. The EDS analysis results showed that the content of metal cations on biochar continued to decrease with aging, indicating that biochar utilized K⁺, Na⁺, Ca²⁺, Mg²⁺, Mn²⁺ to exchange ions with Cd in the soil, thereby adsorbing Cd onto itself. As aging progressed, the ion exchange function of biochar became more thorough, leading to an increase in the proportion of Cd adsorption contributed by the mineral mechanism of biochar. The XRD results also indicated that, as ageing progressed, the KCl frequently found on fresh biochar was converted to SiO₂, which confirmed that metal cations have undergone ion exchange with Cd in the soil, which was attributed to the mineral mechanisms of biochar. Additionally, the higher the percentage of MP500 in the soil, the greater the role of the mineral mechanism, suggesting that ion exchange and mineral precipitation became more dominant in Cd adsorption. By the 180th day of ageing, the mineral mechanism accounted for 51.20 %, 52.14 %, 52.35 %, 53.34 %, 53.41 %, and 54.49 % of Cd adsorption in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500, respectively. When microplastic content in the

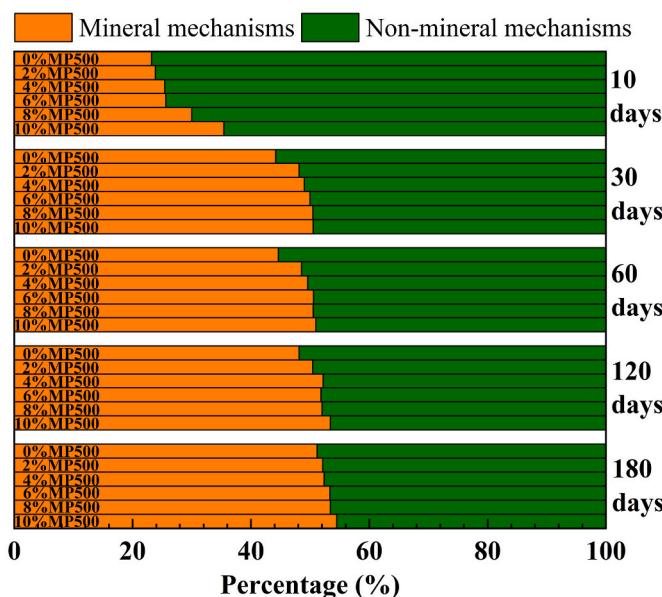


Fig. 6. The contributions of mineral and nonmineral components of MBC to Cd adsorption in soils containing 0 %, 2 %, 4 %, 6 %, 8 %, and 10 % MP500 during ageing times of 10 days, 30 days, 60 days, 120 days, and 180 days.

Notes: MP500 is 500-mesh polyethylene microplastics; MBC is KMnO₄-modified rice straw biochar. The adsorption of acidified biochar can be seen as the contributions of non-mineral components. Moreover, the differences in the adsorption between unacidified and acidified biochars were defined as the contributions of mineral components. Quantify the contribution percentages of mineral mechanisms and non-mineral mechanisms to the adsorption of Cd in soils by biochar, thereby elucidating the roles of mineral mechanisms (ion exchange, mineral precipitation) and non-mineral mechanisms (functional group complexation, other potential mechanisms).

soil increased, the amount of Cd adsorbed by biochar also rose. Initially, the non-mineral mechanism dominated, but its adsorption capacity was limited. As ageing progressed or Cd contamination levels increased, the mineral mechanism gradually became more prominent and played a larger role (Meng et al., 2024a). Therefore, for soils co-contaminated with Cd and microplastics, biochar with a dominant mineral mechanism should be selected for remediation.

4. Conclusions

After co-ageing, a higher concentration of microplastics led to an increase in the pH levels of both the aged soil and biochar. The application of biochar reduced the leaching of Cd from the soil compared to the CK, while also enhancing the proportion of Cd in relatively stable fractions. However, as the percentage of MP500 in the soil rose, the leaching of Cd into the environment also increased; although Cd adsorption capacity of biochar increased, the proportion of relatively stable Cd in soil-biochar samples declined. This indicated that microplastics interfered with biochar's effectiveness in remediating Cd-contaminated soil. Over time, the role of the mineral mechanisms of biochar for Cd adsorption became more significant with ageing. Additionally, a higher MP500 percentage in the soil correlated with a greater contribution from the mineral mechanism in biochar. This study highlighted that Cd adsorbed on microplastics was a greater threat to the agricultural soil environment compared to Cd in soils, which in turn increased the environmental risk of Cd in soils and the difficulty of biochar remediation.

CRediT authorship contribution statement

Zhuowen Meng: Writing – original draft, Formal analysis, Data

curation. Shuang Huang: Writing – review & editing, Resources. Jingwei Wu: Writing – review & editing. Yiyi Deng: Writing – review & editing, Resources.

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. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2025.126655>.

Data availability

Data will be made available on request.

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