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SOIL DEGRADATION CONTROL, REMEDIATION AND RECLAMATION

Calcium-iron composite modified biochar: An effective strategy for Cd passivation and carbon sequestration enhancement

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Abstract

Purpose Calcium-iron composite modified biochar (FeCaBC) exhibits excellent pollutant adsorption capacity, but its synergistic effects on cadmium (Cd)-contaminated soil remediation and greenhouse gas emissions remain unclear. This study aimed to clarify the impacts of FeCaBC on soil available Cd, crop Cd uptake, soil organic carbon (SOC), and soil CO_2 emissions in Cd-contaminated soils.

Materials and methods Soil incubation, CO_2 emissions, and potting experiments were integrated to evaluate the performance of FeCaBC. Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and structural equation modeling (SEM) were used to elucidate the underlying mechanisms.

Results and Discussion FeCaBC application significantly improved soil nutrient availability, increasing available P (114%-186%), available K (48%-84%), and ammonium N (20%-32%). At 0.5%–2% application rate, FeCaBC reduced soil available Cd by 37%-52% and ryegrass Cd content by 10%-31% ($P<0.05$), primarily via promoting Cd transformation from exchangeable to residual fractions. Concurrently, 0.5%-2% FeCaBC increased SOC by 130%-134% and inhibited soil CO_2 emissions by 30%-37% ($P<0.05$). FTIR, XPS, and SEM results indicated that FeCaBC facilitated synergistic Cd immobilization and carbon sequestration through two pathways: (1) surface functional groups mediating Cd complexation and ion exchange; (2) regulating soil physicochemical properties, nutrient cycling, and oxygen-containing functional group proportions to form stable organic complexes.

Conclusions FeCaBC is an effective soil amendment that synchronously remediates Cd-contaminated soil and enhances carbon sequestration by reducing soil available Cd and crop Cd uptake while inhibiting soil CO_2 emissions and increasing soil organic carbon content, making it promising for sustainable remediation of contaminated agricultural soils.

Highlights

- Soil physicochemical property and nutrient availability improved after adding FeCaBC.
- Complexation and ion exchange were the direct pathways for FeCaBC to immobilize Cd.
- The addition of FeCaBC reduced CO_2 emissions by regulating the soil functional groups.
- Cd remediation and CO_2 reduction were simultaneously achieved in FeCaBC treated soil.

Keywords Calcium-iron modified biochar · Cd-contaminated soil · Remediation mechanism · Carbon sequestration · Synergistic effects

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1 Introduction

Soil health is crucial to the sustainable development of society (Anum et al. 2024). However, approximately one-fifth of the world's soil is contaminated with heavy metals caused by human activities such as mining, sewage irrigation, and improper application of fertilizer, further exacerbating the scarcity of agricultural resources (He et al. 2024; Vareda et al. 2019). Cadmium (Cd) is one of the most toxic heavy metals, characterized by high mobility and persistence (Khaliq et al. 2024). Long-term exposure to elevated Cd levels in farmland soils can alter microbial communities, suppress enzyme activities, and reduce soil fertility, thus inhibiting crop growth and constraining agricultural development (Wang et al. 2023a). More importantly, Cd can be transferred to edible crop tissues and enter the human food chain, increasing dietary Cd intake and associated health risks(Chen et al. 2023; Wang et al. 2023a). Therefore, remediating Cd-contaminated soils is essential to reduce Cd transfer from soil to crops and to mitigate human exposure, while maintaining agricultural productivity. Various methods have been applied to the remediation of Cd-contaminated soil, such as electrochemical remediation, in situ remediation, and phytoremediation (Yang et al. 2023). Among these, in situ immobilization has been widely investigated because of its relatively low disturbance and operational feasibility (Anum et al. 2024). Commonly used remediation materials include lime, amendments, attapulgite, sepiolite, and biochar (Jiao et al. 2025; Yang et al. 2023).

Biochar is an effective material for immobilizing heavy metals in soil due to its large specific surface area, porous structure, and abundant active sites (Biswash et al. 2024; Yang et al. 2024a). However, due to the complexity of heavy metal contaminated soil, the application performance and economic benefits of biochar have been restricted (Huang et al. 2021), so there is an urgent need to develop high-performance biochar. Metal oxide modification is an effective approach to enhance biochar performance (Tao et al. 2023). For instance, iron-modified biochar can reduce the mineralization of soil organic carbon (Weng et al. 2022) and the mobility of Cd in soil (Fang et al. 2024). Applying Fe-Zn, Fe-Mn, Fe-S, and Fe-Mg composite-modified biochar have been shown to effectively reduce the available Cd concentration in soil, thereby positively promoting crop yield and quality (Yang et al. 2024b). Nevertheless, the aforementioned modified biochar is generally plagued by issues of potential environmental risks and high production cost. Calcium, as one of the main mineral components in soil, is an essential element for promoting plant growth (Nan et al. 2021). Calcium-modified rice husk biochar could reduce the concentration of available Cd in soil (Zhang et al. 2019) through chemical reactions with heavy metals (Li et al. 2024b). In our previous studies, we successfully prepared high-performance calcium-iron composite modified biochar (FeCaBC) based on machine learning, which can effectively adsorb Cd in aqueous solution through precipitation, complexation, and ion exchange reactions, with an adsorption capacity of up to 78.0 mg/g (Xiang et al. 2024, 2025). However, the application of FeCaBC in Cd-contaminated soils has been scarcely investigated, and its coupled effects on Cd immobilization and soil carbon dynamics remain unclear.

Single Fe or Ca modified biochars exhibit potential for Cd passivation or carbon sequestration individually, but suffer from the limitations of single function and unexploited synergistic effects. Fe-modified biochars focus on Cd adsorption and immobilization but have limited effects on improving soil nutrients (Fang et al. 2024). While, Ca-modified biochars can ameliorate soil alkaline environment but show weak organic carbon stabilization capacity (Li et al. 2024b). Existing studies on Fe-Ca composite modified biochars have only focused on the Cd adsorption behavior in aqueous solutions (Xiang et al. 2024), without revealing its synergistic mechanism for simultaneous Cd passivation, carbon sequestration and soil fertility improvement in Cd-contaminated soils, nor clarifying its regulatory effect on soil CO_2 emissions and key influencing pathways.

Due to the high CO_2 emissions and limited carbon cycle in heavy metal-contaminated soil (Wang et al. 2025a), increasing carbon sequestration while remediating contaminated soil can contribute to more sustainable remediation by simultaneously reducing Cd risks and improving soil carbon retention / reducing CO_2 emissions. The application of biochar could inhibit organic carbon mineralization and improve carbon sequestration on soil by forming stable complexes with soil organic carbon (Si et al. 2024), and increasing persistent carbon and microbial carbon metabolism (Han et al. 2020; Ji et al. 2023). Iron-modified biochar has a large specific surface area (Mei et al. 2021), and can further regulate the mineralization rate of soil organic carbon (SOC) by modulating microbial-mediated SOC mineralization (Wang et al. 2023b). Biochar often contains alkaline ash components such as CaO/$CaCO_3$. Ca loaded on biochar- can further increase alkaline sites, which may facilitate inorganic carbon formation (e.g., carbonate species) under suitable conditions (Othman et al. 2021). Calcium/iron-loaded biochar has been used in studies related to soil quality improvement, which can enhance soil aggregate stability(Buss et al. 2022) and stabilize SOC (Liu et al. 2022). However, current research has only separately discussed the effects of FeCaBC on soil quality. However, it remains unclear how FeCaBC amendment influences SOC dynamics and CO_2 emissions in Cd-contaminated soil.

In this study, the novel Fe-Ca composite modified biochar prepared was applied to the remediation of Cd-contaminated

soil to investigate the effects and mechanisms on Cd fraction and CO_2 emissions in soil through incubation experiments, respiration experiments, potting experiments, and characterization. The objectives of this study were (1) to investigate the effects of FeCaBC on soil physicochemical properties, fertility, available Cd content, Cd faction distribution, and Cd accumulation in ryegrass; (2) to study the effects of FeCaBC on soil organic carbon content and CO_2 emissions; (3) to analyze the key factors and pathways affecting the reduction of available Cd and CO_2 by FeCaBC through correlation analysis, structural equation modeling (SEM) and characterization techniques. This study is expected to provide guidance for the application of biochar in soil remediation and carbon sequestration.

Specifically, the following hypotheses are tested: (1) FeCaBC will demonstrate significant performance in reducing the Cd bioavailability and promoting its transformation into stable fraction; (2) FeCaBC will increase soil carbon content and reduce CO_2 emissions; (3) FeCaBC may remediate Cd-contaminated soil through its structural characteristics and by influencing soil physical and nutrient conditions.

2 Materials and methods

2.1 Reagents and soils

The reagents of Cd $(NO_3)_2 \cdot 4\ H_2O$, NaOH, HNO_3, Fe $(NO_3)_3$ and $CaCl_2$ were purchased from Tianjin Jiangtian Chemical Co., Ltd. The biomass of wheat straw was collected from farmland in the Binhai New Area of Tianjin.

A background (uncontaminated) agricultural topsoil (0–20 cm) was collected from Neihuang County, Henan Province. The background soil used in this study was collected from Henan Province, a major agricultural and grain-producing region in China, with a near-neutral pH of 7.45, representing a typical soil type widely distributed in many agricultural areas. Despite this relatively high pH, the artificially spiked soil exhibited a high DTPA-extractable Cd concentration (1.32 mg/kg), resulting in measurable Cd accumulation in ryegrass. Thus, this soil represents a relevant scenario for evaluating the immobilization efficacy of amendments under near-neutral conditions, where conventional liming may exhibit limited effectiveness(Bolan et al. 2014). The soil was air-dried, sieved, and then artificially spiked with Cd $(NO_3)_2 \cdot 4\ H_2O$ solution. The spiked soil was aged for 30 days at room temperature (mixed every 5 days) before use. The aged Cd-contaminated soil was used for the experiment, with a total Cd content of 1.92 mg/kg and available Cd content of 1.32 mg/kg.

2.2 Preparation of biochar

Biochar (BC): Biochar was prepared using wheat straw as the biomass at a pyrolysis temperature of 500 °C, a heating rate of 5 °C/min, and a pyrolysis time of 2 h.

Iron-modified biochar (FeBC): The biomass of wheat straw was immersed into the configured 0.5 mol/L $Fe(NO_3)_3$ solution with the mass ratio of biomass: iron ions of 1:4, and then stirred for 4 h. After stirring, the mixture was filtered and dried in an oven at 60 °C. The dried biomass was then placed in a tube furnace and pyrolyzed at 500 °C for 2 h at a heating rate of 5 °C/min to yield iron-modified biochar, named FeBC.

Calcium-modified biochar (CaBC): The biomass of wheat straw was immersed into the configured 0.8 mol/L $CaCl_2$ solution with the mass ratio of biomass: calcium ions of 1:1, and then stirred for 4 h. Then it was pyrolyzed under the same pyrolysis conditions as FeBC to obtain calcium-modified biochar, named CaBC.

Iron-calcium composite modified biochar (FeCaBC): The wheat straw biomass was placed into the mixed solution (containing 0.5 mol/L $Fe(NO_3)_3$ and 0.8 mol/L $CaCl_2$) with the mass ratio of biomass: iron ions: calcium ions of 1:4:1. Under the same pyrolysis conditions as described above, iron-calcium composite modified biochar was obtained, designated as FeCaBC (Xiang et al. 2024).

2.3 Soil culture experiment

2000 g of Cd-contaminated soil was accurately weighed and placed in a plastic basin and then mixed thoroughly with remediation materials (BC, FeBC, CaBC, and FeCaBC) at dosage of 0.5%, 1.0%, and 2.0%, respectively. The experiment was conducted using four types of materials, with a total of 13 treatment groups: CK, 0.5% BC, 1% BC, 2% BC, 0.5% FeBC, 1% FeBC, 2% FeBC, 0.5% CaBC, 1% CaBC, 2% CaBC, 0.5% FeCaBC, 1% FeCaBC, and 2% FeCaBC. Three parallel experiments were set up for each treatment group. The soil was watered regularly to maintain the moisture content at approximately 30% during incubation. The soil incubation period was 60 days, and soil samples were collected for analysis at 5, 10, 30, and 60 days. Soil moisture was maintained at ~30% of field capacity to keep the incubation under aerobic conditions and to minimize waterlogging-related variability. Soil moisture was adjusted by weighing and adding deionized water regularly.

2.4 Soil respiration experiment

Soil respiration was quantified using the traditional titration method and the improved Hopkins technique (Hopkins et al. 1988). The incubation was conducted at a constant

temperature of 25 ± 1 °C with the headspace volume controlled at 750 ± 10 mL in the sealed glass bottle. During incubation, soil moisture was maintained at 30% of field capacity by weighing and replenishing deionized water every 2 days to compensate for evaporation loss. Each bottle was opened briefly, and water was added rapidly within 1 min to minimize gas exchange and ensure the accuracy of CO_2 emissions measurement. Briefly, 50 g of cadmium-contaminated soil was placed in a 100 mL centrifuge tube, with 0.5%, 1%, and 2% of BC, FeBC, CaBC, and FeCaBC, respectively. The centrifuge tube was suspended in a glass bottle containing a 0.05 mol/L NaOH solution (no contact with soil or bottle walls). The glass bottle was sealed with a rubber stopper and paraffin wax, and a leak test was performed before incubation by injecting N_2 gas (a concentration change of < 1% after 24 h was considered qualified). A visual leak check was also conducted at each NaOH replacement time point during incubation. 0.05 mol/L NaOH in a small beaker was removed on days 5, 10, 30, and 60, then used to calculate CO_2 emissions by back titration with 0.05 mol/L HCl (three parallel titrations for each sample, relative standard deviation < 2%). A NaOH solution placed in an empty glass bottle was subjected to the same treatment to correct for environmental CO_2. The formula for calculating soil CO_2 emissions is as follows:

$$CO_2(mg/kg) = [(V_0 - V) \times C \times M]/m$$

Where, V_0 (mL) represents the volume of standard hydrochloric acid consumed during blank titration; V (mL) represents the volume of standard hydrochloric acid consumed for each treatment group; C (mol/L) represents the concentration of standard hydrochloric acid; M is the molar mass of CO_2 (M (1/2 CO_2) = 22 mg $mmol^{-1}$); m is the soil mass of treatment. Values reported are cumulative CO_2 production within each time interval Δt and converted to hourly flux ($mg \cdot kg^{-1} \cdot h^{-1}$) by dividing by the corresponding hours in the interval.

2.5 Pot experiment

Two remediation materials (BC and FeCaBC) with three dosage (0.5%, 1%, and 2%) and a control group were set up. Two kilograms of cadmium-contaminated soil was accurately weighed and placed in a plastic basin and then mixed evenly with BC or FeCaBC. The experiment consisted of 7 treatment groups: CK (control group), 0.5% BC, 1% BC, 2% BC, 0.5% FeCaBC, 1% FeCaBC, and 2% FeCaBC. Ryegrass seeds were sown on moistened sterile gauze and incubated at room temperature for 6 days. After germination, uniform seedlings were transplanted into flower pots, with 12 seedlings in each pot. The plants were harvested after four weeks of growth. The plant samples were rinsed repeatedly with deionized water and oven-dried at 105 °C until constant weight for cadmium content analysis. Each treatment was triplicated. No additional N, P, or K fertilizers were applied during the pot experiment to avoid confounding effects on Cd uptake and soil nutrient dynamics.

2.6 Analysis and characterization

Soil pH and cation exchange capacity (CEC) were measured using a pH meter (soil-to-water ratio = 1:2.5) and the hexamine cobalt trichloride solution-spectrophotometric method, respectively (Sumner and Miller 1996). Soil organic carbon (SOC) was determined by wet oxidation method (Serrano et al. 2023). The content of available Cd in soil was extracted and measured using diethylenetriaminepentaacetic acid (DTPA) (Lindsay and Norvell 1978). Soil available P content was determined using the molybdenum antimony colorimetric method with a 0.5 mol/L $NaHCO_3$ (Li et al. 2019). Concentration of available K was analyzed by the flame atomic absorption spectrometer (FP640, Shanghai Xijin Instruments Co., Ltd., Shanghai) (Thomas 1982). Potassium chloride extraction-indophenol blue colorimetric method was used to determine the content of ammonium N in soil (Mulvaney 1996). Five fractions of Cd in soil were extracted using the Tessier sequential extraction method (Tessier et al. 1979), namely exchangeable (EX), carbonate-bound (CB), Fe-Mn oxide-bound (OX), organic matter-bound (OM), and residual (RS) fractions. The Cd content in plant was determined by flame atomic absorption spectrophotometry (FP640, Shanghai Xijin Instruments Co., Ltd., Shanghai) after digestion with HCl-HNO_3 (Gonçalo Filho et al. 2020).

Two methods were employed to evaluate the stability of FeCaBC. (1) Chemical stability: FeCaBC was subjected to chemical oxidation treatment in a 5% H_2O_2 solution at a constant temperature of 80 °C for 48 h, followed by drying in an oven at 105 °C for 12 h (Liang et al. 2021). The carbon loss rate represents the chemical stability of FeCaBC, which was calculated by measuring the total carbon content of FeCaBC before and after oxidation treatment using elemental analysis (EA, UNICUBE, Germany). In addition, the thermal stability of the material was evaluated based on the thermogravimetric loss characteristics (Zhong et al. 2023).

Thermogravimetric and differential thermogravimetric (TG/DTG) analyses, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were conducted on four materials (BC, FeBC, CaBC, FeCaBC), the original Cd-contaminated soil, and the soil samples amended with these four materials at 0.5%, 1%, and 2% application rates after 60 days of incubation. Specifically, FTIR measurements on a TENSOR27 spectrometer

(Germany) in the 800–4000 cm^{-1} range were used to identify the surface functional groups of the materials and materials-amended soils. TG/DTG curves of the above samples were acquired with a HS-TGA-301 thermogravimetric analyzer (Ltd., Shanghai). The chemical composition of the samples was further analyzed by an XPS photoelectron spectrometer (Thermo Scientific, USA, ESCALAB 250XI) to characterize their surface properties and carbon functional groups.

2.7 Statistical analysis

Data processing and analysis were performed using Excel 2010, Data processing and visualization were performed using Excel 2010 and Origin 2021. One-way ANOVA was performed using IBM SPSS (23.0) to assess significant differences. Prior to statistical analysis, the normality of all data was verified via the Shapiro-Wilk test, and the homogeneity of variances was examined using Levene's test. $P<0.05$ was considered statistically significant.

For time-series data (sampled at 5, 10, 30, and 60 days), time points were treated as repeated measures. Post-hoc multiple comparisons were conducted using the Tukey's HSD test, and the Bonferroni correction was applied to adjust for multiple testing at different time points to control the family-wise error rate. The independence of soil samples at each time point was ensured by using separate, non-overlapping soil subsamples for each sampling event, with three biological replicates maintained for all treatments at every time point.

Structural equation modeling (SEM) is a multivariate statistical technique that integrates parametric analysis and path analysis to quantitatively investigate the interactions among multiple variables. To explore the direct and indirect relationships between soil physicochemical properties, cadmium (Cd), and CO_2 emissions, a structural equation model was constructed in this study. The model was evaluated using goodness-of-fit index (GFI), adjusted goodness-of-fit index (AGFI), and root mean square error (RMSE) indicators, with subsequent analysis of the interactions among factors. A good model fit was indicated when χ^2/df ranged from 0 to 2, GFI and AGFI were close to 1, and RMSE was close to 0.

3 Results

3.1 Effects of amendments on soil physicochemical properties

3.1.1 Soil pH

The effect of different remediation materials on soil pH value is shown in Fig. 1(a). The pH of the control soil (CK) ranged from 7.45 to 7.61 and fluctuated over the incubation period. By day 60, the soil pH in the 2% BC, FeBC, CaBC, and FeCaBC treatments had increased by 0.17, 0.23, 0.18, and 0.27 pH units, respectively, compared to the values observed on day 5. Application of four biochar (BC, FeBC, CaBC, and FeCaBC) resulted in elevated soil pH. Among these, the FeCaBC treatment led to the most pronounced increase (0.29–0.57 pH units) ($P<0.05$), followed by the CaBC (0.23–0.42 pH units), FeBC (0.20–0.41 pH units), and BC (0.13–0.32 pH units). Soil pH exhibited a positive correlation with the application rate of the amendments. Specifically, when FeCaBC was applied at 0.5%, 1%, and 2%, the soil pH increased by 0.29–0.44, 0.30–0.53, and 0.33–0.57 pH units, respectively, compared to the CK ($P<0.05$).

3.1.2 Soil CEC

The effect of remediation materials on soil cation exchange capacity (CEC) is presented in Fig. 1(b). The CEC values of soil in all treatments increased over the incubation period. By day 60, the CEC values in the 2% BC, FeBC, CaBC, and FeCaBC treatments reached 14.51, 18.31, 17.93, and 19.60 cmol/kg, respectively, representing increases of 57%, 98%, 94%, and 113% compared to the CK. Overall, adding 0.5%-2% FeCaBC resulted in the most significant enhancement in soil CEC (35%-112%) ($P<0.05$), followed by 0.5%-2% FeBC (22%-99%), 0.5%-2% CaBC (18%-94%), and 0.5%-2% BC (3%-57%). Consistent with the trend in soil pH, soil CEC increased with rising application rates of remediation materials. For instance, the contents of soil CEC in 0.5%, 1%, and 2% FeCaBC treatments were 84%, 98%, and 113% higher than that of the CK on the 60th day of incubation, respectively ($P<0.05$).

3.1.3 Available P, available K, and ammonium N in soil

On day 60 of cultivation, the effects of BC, FeBC, CaBC, and FeCaBC addition on soil available nutrient contents are presented in Table 1. Compared with the CK, biochar addition increased the contents of soil available P, available K, and ammonium N. High-dose remediation materials had a greater effect on soil available nutrients than low-dose

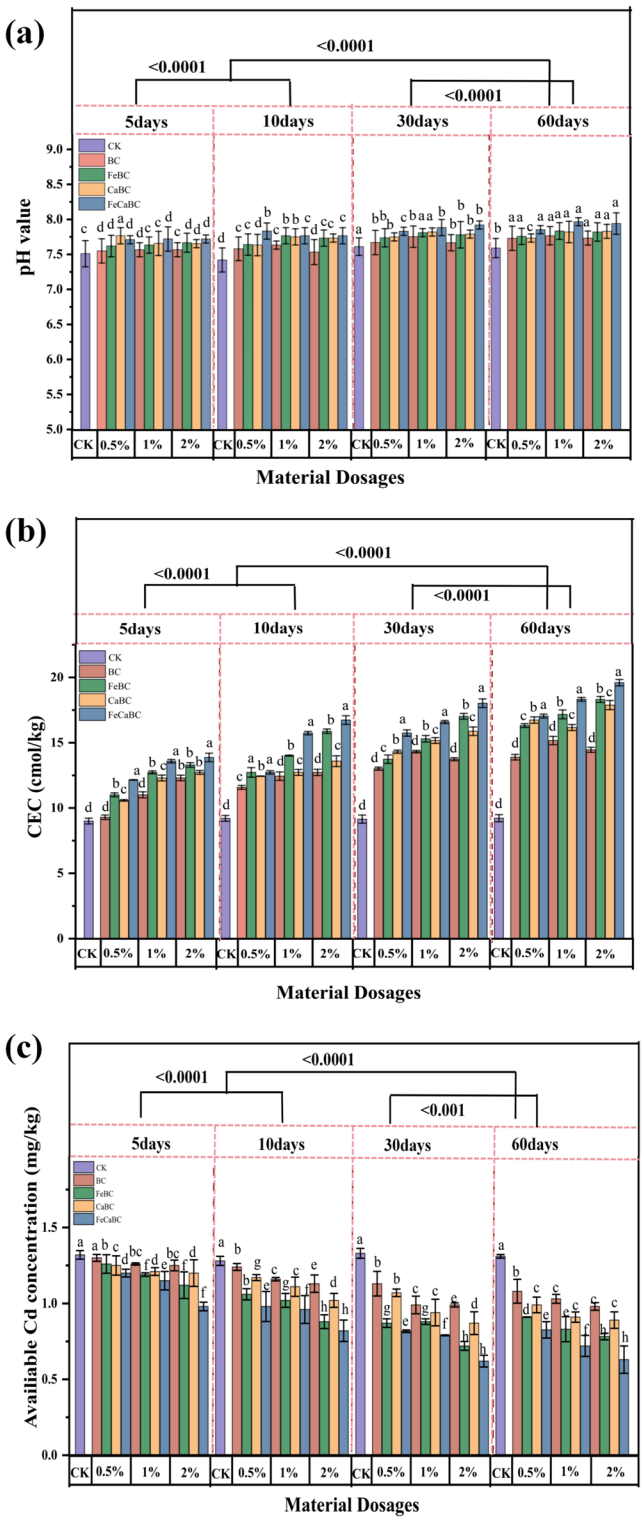

Fig. 1 Effects of 0.5%-2% BC, FeBC, CaBC and FeCaBC on soil pH (**a**), CEC (**b**) and available Cd content (**c**)

Table 1 Effects of 0.5%–2% BC, FeBC, CaBC and FeCaBC on soil available P, available K and ammonium N content

Treatments	Available *P* (mg/kg)	Available K (mg/kg)	Ammonium *N* (mg/kg)
CK	22.53 ± 0.76a	137.30 ± 0.21a	11.14 ± 0.15a
0.5%BC	24.32 ± 0.59b	144.23 ± 0.15b	11.32 ± 0.27a
1%BC	38.36 ± 0.30 h	172.23 ± 0.22d	11.34 ± 0.12a
2%BC	35.27 ± 0.32f	195.28 ± 0.31e	11.62 ± 0.16b
0.5%FeBC	25.24 ± 0.50c	150.87 ± 0.25b	11.36 ± 0.46a
1%FeBC	33.25 ± 0.40d	193.05 ± 0.36e	11.49 ± 0.25a
2%FeBC	38.89 ± 0.10i	205.50 ± 0.18 g	12.30 ± 0.40b
0.5%CaBC	37.32 ± 0.12 g	160.05 ± 0.22c	11.17 ± 0.25a
1%CaBC	34.63 ± 0.62e	170.03 ± 0.25d	12.54 ± 0.26c
2%CaBC	45.56 ± 0.18j	205.53 ± 0.51 h	12.63 ± 0.25b
0.5%FeCaBC	48.21 ± 0.20k	203.63 ± 0.15f	13.32 ± 0.17f
1%FeCaBC	56.77 ± 0.61k	219.73 ± 0.10i	14.62 ± 0.20e
2%FeCaBC	64.48 ± 0.53k	253.20 ± 0.45j	14.68 ± 0.32d

treatments. Specifically, relative to the 0.5% BC, FeBC, CaBC, and FeCaBC groups, the soil available P content in the 2% BC, FeBC, CaBC, and FeCaBC groups increased by 45%, 54%, 22%, and 34%, respectively ($P < 0.05$). Similar trends were observed for soil available K and ammonium N contents across all treatment groups, with their concentrations increasing in response to higher application rate of remediation materials.

Compared with the BC treatment, the addition of FeBC, CaBC, and FeCaBC increased the soil available P content to 38.89, 45.56, and 64.48 mg/kg, respectively; the readily available K content to 205.50, 205.53, and 253.20 mg/kg, respectively; and the ammonium N content to 12.30, 12.63, and 14.68 mg/kg, respectively. Among these amendments, the application of 0.5%–2% FeCaBC resulted in the most pronounced improvement in soil fertility, increasing the contents of soil available P, available K, and ammonium N by 114%-186%, 48%-84%, and 19%-31%, respectively ($P < 0.05$).

3.2 Effects of amendments on soil Cd availability and fractions

3.2.1 Available Cd content in soil

The toxicity of heavy metals to plants and microorganisms depends on their bioavailable fractions. The content of bioavailable heavy metals reflects the actual contamination level of soil and its potential risk to plants (Zhong et al. 2023). As shown in Fig. 1(c), the DTPA-extractable Cd (DTPA-Cd) contents in the BC, FeBC, CaBC, and FeCaBC treatments gradually decreased with incubation time, reaching the lowest level by day 30 and stabilizing thereafter. Compared with the control group, the DTPA-Cd contents in soil treated with 0.5%-2% BC, FeBC, CaBC, and

FeCaBC decreased by 2%-26%, 5%-41%, 5%-33%, and 9%-52%, respectively ($P<0.05$). The immobilization effect of FeCaBC on soil available Cd was significantly superior to that of BC, FeBC, and CaBC treatments. After 60 days of incubation, the DTPA-Cd contents in soil treated with 0.5%, 1%, and 2% FeCaBC were 0.83 mg/kg, 0.72 mg/kg, and 0.63 mg/kg, respectively, corresponding to reductions of 37%, 45%, and 52% compared to the CK ($P<0.05$).

3.2.2 Distribution of Cd fractions in soil

The chemical fractions of heavy metals in soil are a crucial factor determining their toxicity to crops (Qin et al. 2024). The effect of adding remediation materials on the distribution of Cd fractions in soil is shown in Fig. S1. In the CK, the fractions of Cd in soil were distributed as follows: exchangeable (EX-Cd) 58%, carbonate-bound (CB-Cd) 21%, iron-manganese oxide-bound (OX-Cd) 14%, organic matter-bound (OM-Cd) 7%, and residue (RS-Cd) 1%. Cadmium was predominantly present in the exchangeable fraction, which facilitates its uptake by crops. After adding 0.5%-2% BC, FeBC, CaBC, and FeCaBC, the content of EX-Cd reduced by 16%-19%, 17%-31%, 16%-24%, and 22%-34%, respectively ($P<0.05$), while RS-Cd increased by 67%-75%, 90%-93%, 67%-89%, and 86%-95%, respectively ($P<0.05$). In the 0.5%-2% FeCaBC treatments, OX components of Cd increased by 43%, 36%, and 37%, indicating that the addition of FeCaBC promotes the fraction conversion from EX-Cd into RS-Cd and OX-Cd, which was consistent with the mechanism of Cd adsorption to Fe/Mn oxides and incorporation into stable geochemical phases, thereby reducing the mobility of Cd in the soil.

3.2.3 Cadmium content in ryegrass

Biochar can influence Cd accumulation in plants by altering the fractions distribution and bioavailability of Cd in soil. The effects of amendments on Cd accumulation in ryegrass are presented in Fig. S2. Following the application of 0.5%-2% FeCaBC, the Cd content in the aboveground parts of ryegrass ranged from 0.75 to 0.97 mg/kg, corresponding to a reduction of 10%-31% compared to CK ($P<0.05$). The most significant reduction in Cd accumulation in ryegrass was observed at a FeCaBC application rate of 2%. In addition, this study did not determine the biomass parameters of ryegrass (shoot/root dry weight, plant height). Future research should investigate the effects of FeCaBC on plant growth.

3.3 Effects of amendments on soil organic carbon and CO_2 emissions

3.3.1 Soil CO_2 emissions

The effects of biochar and modified biochar on soil CO_2 emissions are presented in Table 2 Soil CO_2 emissions in all treatments decreased over time, reaching a minimum at 30 days and stabilizing thereafter. On day 30, the CO_2 emissions in the 0.5%-2% BC, FeBC, CaBC, and FeCaBC treatments were 0.86–0.89 $mg\cdot(kg\cdot soil)^{-1}\cdot h^{-1}$, 0.77–0.80 $mg\cdot(kg\cdot soil)^{-1}\cdot h^{-1}$, 0.81–0.85 $mg\cdot(kg\cdot soil)^{-1}\cdot h^{-1}$, and 0.62–0.68 $mg\cdot(kg\cdot soil)^{-1}\cdot h^{-1}$, respectively, representing reductions 9%-12%, 18%-21%, 14%-18%, and 30%-37% compared to CK ($P<0.05$). Soil CO_2 emissions decreased with increasing FeCaBC application rates. The soil CO_2 emissions in the 2% BC, FeBC, CaBC, and FeCaBC treatments were significantly lower than those in the 0.5% and 1% application rate treatments. Obviously, the efficacy in reducing CO_2 emissions followed the order: FeCaBC > FeBC > CaBC > BC. On day 30, the application of 0.5%, 1%, and 2% FeCaBC reduced soil CO_2 emissions to 0.68, 0.62, and 0.63 $mg\cdot(kg\cdot soil)^{-1}\cdot h^{-1}$, respectively, with the lowest soil CO_2 emissions observed in the 1% FeCaBC treatment.

Table 2 The CO_2 emissions of soil at 5, 10, 30, and 60 days of incubation with amendments

Treatments	Soil CO_2 emissions ($mg\cdot kg^{-1}\cdot h^{-1}$)			
	5 days	10 days	30 days	60 days
CK	3.00 ± 0.05a	2.13 ± 0.04a	0.98 ± 0.04a	1.15 ± 0.04a
0.5%BC	2.78 ± 0.04b	1.96 ± 0.03b	0.87 ± 0.03b	1.00 ± 0.03b
1%BC	2.75 ± 0.04b	1.93 ± 0.03b	0.89 ± 0.03b	1.02 ± 0.03b
2%BC	2.68 ± 0.03b	1.91 ± 0.03b	0.86 ± 0.02b	0.98 ± 0.02b
0.5%FeBC	2.73 ± 0.03b	1.77 ± 0.02c	0.80 ± 0.02c	0.95 ± 0.02bc
1%FeBC	2.66 ± 0.03bc	1.72 ± 0.02 cd	0.77 ± 0.03 cd	0.84 ± 0.02 cd
2%FeBC	2.42 ± 0.03 cd	1.66 ± 0.02d	0.79 ± 0.02 cd	0.88 ± 0.02c
0.5%CaBC	2.77 ± 0.04b	1.83 ± 0.03bc	0.83 ± 0.03bc	0.90 ± 0.03bc
1%CaBC	2.70 ± 0.03b	1.87 ± 0.03b	0.81 ± 0.02c	0.88 ± 0.02c
2%CaBC	2.63 ± 0.03bc	1.83 ± 0.03bc	0.85 ± 0.03b	0.87 ± 0.02c
0.5%FeCaBC	2.14 ± 0.02de	1.73 ± 0.02 cd	0.68 ± 0.02d	0.79 ± 0.02d
1%FeCaBC	1.98 ± 0.02e	1.62 ± 0.02d	0.62 ± 0.01e	0.75 ± 0.01d
2%FeCaBC	1.88 ± 0.02e	1.55 ± 0.02d	0.63 ± 0.02e	0.75 ± 0.01d

3.3.2 Soil organic carbon content

The effect of remediation materials on soil organic carbon (SOC) content is presented in Fig. 2. The content of SOC in CK ranged from 8.17 to 8.31 g/kg. The total carbon contents of BC, FeBC, CaBC and FeCaBC were 52%, 50%, 52% and 50% (Table S1). The direct carbon input of the four biochar was 2.490–2.615 g/kg, 4.980–5.230 g/kg and 9.960–10.460 g/kg at 0.5%, 1% and 2% application rates, respectively. Moreover, the carbon input of 0.5%, 1% and 2% FeCaBC to soil was 2.510 g/kg, 5.020 g/kg and 10.040 g/kg respectively. Following the addition of all four biochar, the soil organic carbon (SOC) content increased rapidly within 10 days (reaching approximately double that of the CK), continued to rise thereafter, and peaked at 30 days. After 30 days, the soil carbon pool reached a new balance, and a small amount of labile organic carbon underwent moderate mineralization, leading to a slight decrease in SOC. However, the excellent chemical and thermal stability of FeCaBC strongly inhibited the excessive mineralization of SOC (Yang et al. 2022), and its content remained significantly higher than that of the control group throughout the incubation period, which is consistent with the observations in relevant studies (Ji et al. 2023). Furthermore, the content of soil organic carbon improved in the treatments with 0.5%-2% BC, FeBC, CaBC, and FeCaBC, with increases of 50% to 95%, 73% to 120%, 51% to 113%, and 130% to 134%, respectively ($P<0.05$). The measured SOC increase in each treatment was slightly higher than the direct carbon input of biochar, and the difference likely represents the sum of soil native organic carbon immobilization amount and microbial biomass carbon increment, which verified the rationality of the SOC dynamic change in this study. The observed SOC increase partly reflects the direct carbon input from biochar addition. Among all materials, the addition of FeCaBC significantly outperformed BC, FeBC, and CaBC in enhancing soil SOC.

A simple temporal carbon balance was established for carbon accounting and CO_2 source apportionment. Exogenous carbon input from 0.5%, 1.0%, and 2.0% FeCaBC was 2.51, 5.02, and 10.04 g/kg soil, respectively. After 60 days, SOC in soil treated by FeCaBC increased by 130%-134% relative to CK. The CO_2 emissions reported herein represent cumulative fluxes over each interval between NaOH trap replacements (at 5, 10, 30, and 60 days), rather than the instantaneous fluxes. Cumulative CO_2-C emissions were reduced by 30%-37% in FeCaBC treatments at day 30, and total CO_2-C loss was much lower than exogenous carbon input.

3.4 Characterization analysis

The physicochemical properties of the biochar are summarized in Table S1. BC exhibited the highest C content (59.06%), while the lower C, H, N and S contents in FeBC, CaBC and FeCaBC suggested that Fe/Ca loading enhanced biochar aromaticity. Fe $(NO_3)_3$ served as an Fe precursor; nitrate decomposes during pyrolysis, while Fe is retained on the biochar matrix as confirmed by FTIR/XPS. BC and CaBC had relatively low O contents (8.24% and 5.89%),

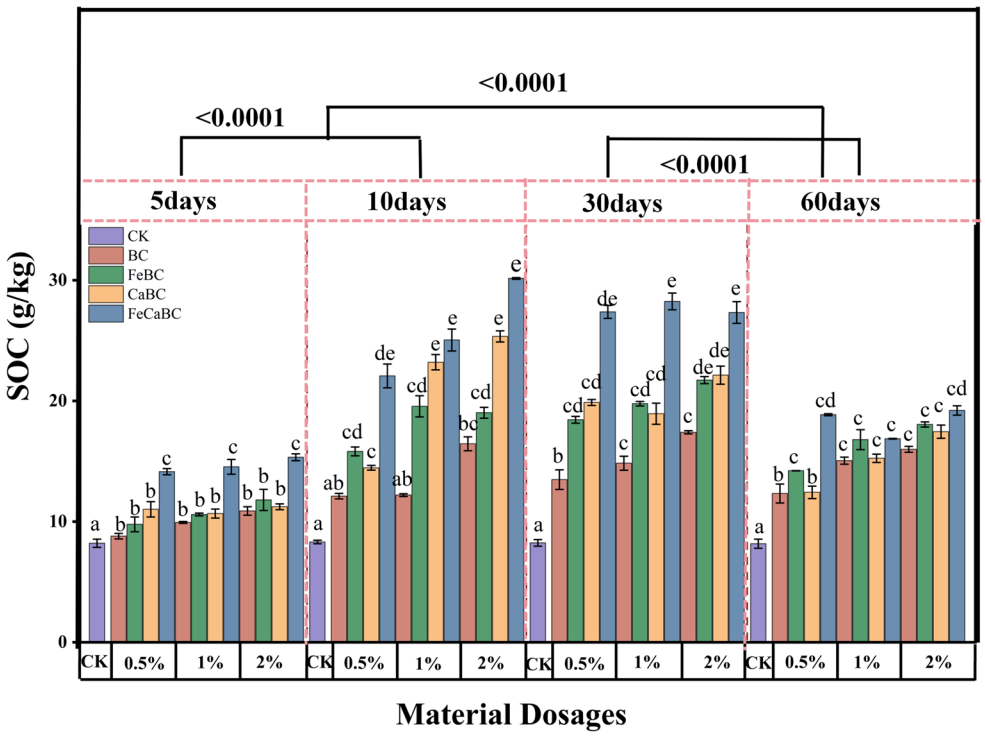

Fig. 2 Effects of 0.5%-2% BC, FeBC, CaBC and FeCaBC on soil organic carbon (SOC) content

whereas FeBC and FeCaBC showed notably higher O contents (11.83% and 10.54%), indicating abundant oxygen-containing functional groups. Successful Fe/Ca loading was confirmed by the high Fe content in FeBC (16.54%) and FeCaBC (19.27%), and high Ca content in CaBC (4.17%) and FeCaBC (4.88%), with BC containing no detectable Fe or Ca. The specific surface area of BC was only 14.53 m^2/g, but modification drastically increased the Sa of FeBC (191.04 m^2/g), CaBC (175.41 m^2/g) and FeCaBC (141.80 m^2/g)—values far exceeding those of previously reported Ca/Fe biochar(Zhang et al. 2023). This Sa increase was attributed to Fe/Ca oxides providing active adsorption sites, while the lower Sa of FeCaBC compared to FeBC and CaBC was likely caused by pore clogging from the dual modification reagents (Li et al. 2024a).

By comparing the FTIR and XPS spectra of soil treated with biochar and modified biochar, the mechanisms underlying their carbon sequestration and pollution reduction effects were analyzed. Unamended Cd-contaminated soil (CK) was not included in the spectral characterization of Fig. 3, as the strong background signals of native soil components would mask the characteristic functional group peaks derived from biochar materials, which is not conducive to clarifying the interaction mechanism between biochar and soil in Cd passivation and carbon sequestration. As shown in Fig. 3(a), the FTIR spectra of BC, FeBC, CaBC, and FeCaBC exhibit characteristic peaks at ~3450, ~2925, ~1543, ~1377, ~1071, and ~788 cm^{-1}, which were assigned to the -OH, -CH_3, C=C/C=O, C-O, C-O-C, and -CH groups, respectively(Xiang et al. 2024). Additionally, FeBC and FeCaBC exhibited Fe-O vibration peaks at 570 cm^{-1}, while CaBC and FeCaBC showed features associated with Ca-O. After 60 days of incubation, the treated soils displayed pronounced absorption peaks at 3707, 2980, 1452, 1027, and 762 cm^{-1} (Fig. 3(a), corresponding respectively to the stretching vibrations of -OH from external hydroxylation, -OH from free or intermolecular hydrogen-bonded groups in phenols and alcohols, C=C of aromatic ring, C-O in phenols and hydroxyl groups, and halogenated compounds (He et al. 2025). These functional groups are associated with the introduction of FeCaBC, which increases the surface content of phenolic hydroxyl groups, alcohol compounds, and

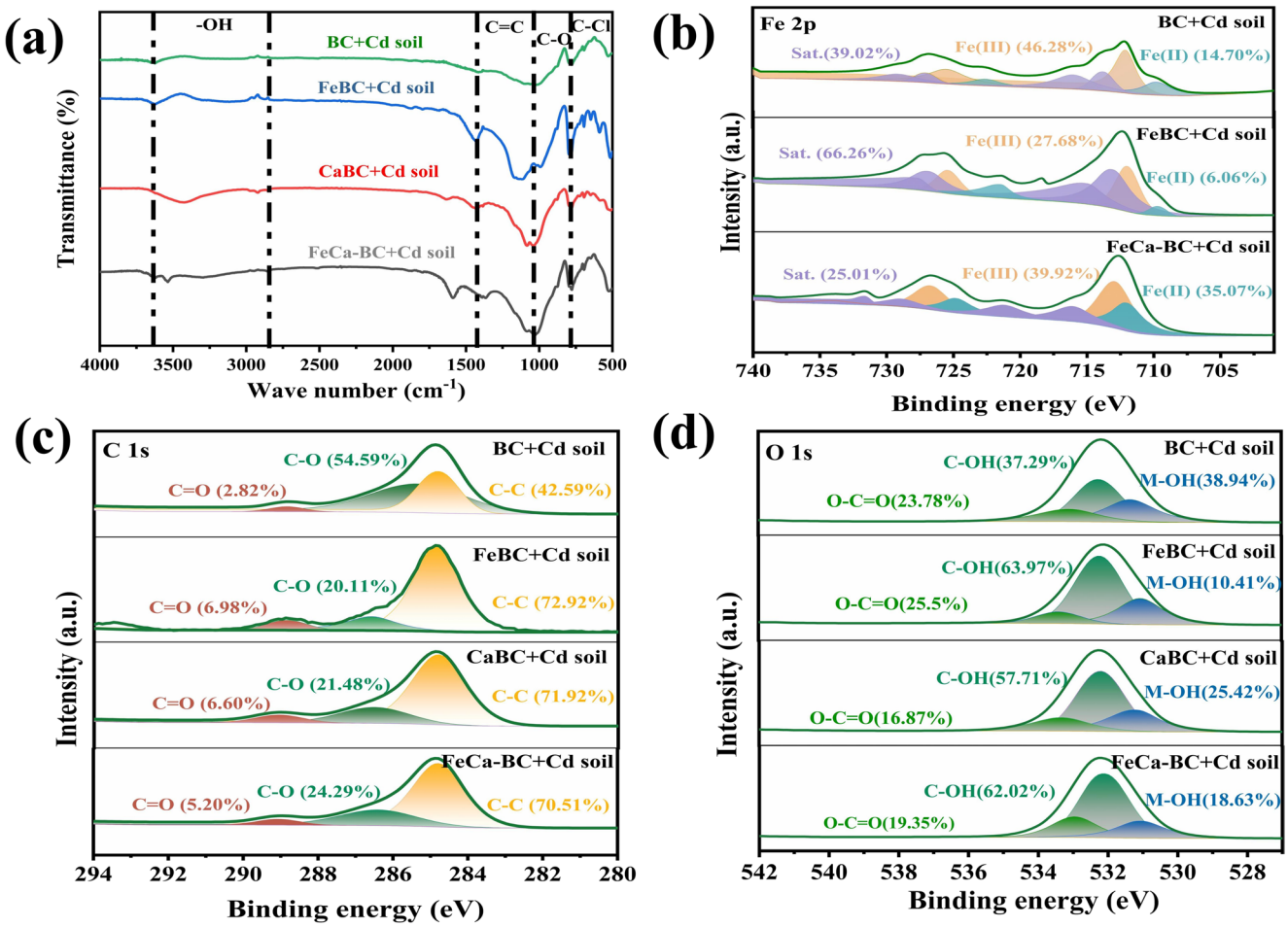

Fig. 3 FTIR spectra (**a**) and Fe 2p (**b**), C 1s (**c**), O 1s (**d**) XPS spectra of soil amended with 0.5%-2% BC, FeBC, CaBC and FeCaBC and incubated for 60 days

microbial-secreted polysaccharide extracellular polymers (Chiaramonti et al. 2024). Notably, the most intense peaks observed in the FeCaBC-treated soil indicates a pronounced effect in enhancing heavy metal stability.

In the XPS C 1s spectrum (Fig. 3(c), peaks were observed at about 284.80 eV, 286.45 eV, and 289.79 eV corresponding to C-C, C-O, and O-C=O bonds, respectively. The O 1s spectrum (Fig. 3(d) marked that the M-OH, C-OH, and O-C=O groups were at about 531.09 eV, 532.18 eV, and 533.75 eV in FeBC, CaBC, and FeCaBC (Tan et al. 2022). For the Fe 2p spectrum (Fig. 3(b), the detection of Fe $2p^{3/2}$ (711.1 eV) and Fe $2p^{1/2}$ (725.8 eV) peaks in FeBC and FeCaBC indicates the presence of Fe (III) and Fe (II), which provide redox active sites for the immobilization of Cd. This represents an important XPS characteristic for the synergistic effect of Fe on Cd passivation. After application of CaBC, FeBC, and FeCaBC to the soil, the XPS spectra exhibited changes. In the FeCaBC-treated soil group, the atomic ratio of $2p^{3/2}$ decreased from 46% to 40%, possibly due to the transfer of π-electrons from C-O-Fe to Fe (Kang et al. 2023). Additionally, the proportions of C-O and C=O in soil added FeCaBC decreased from 37% to 13% to 24% and 5%. The decrease in the relative content of oxygen-containing functional groups suggests that oxygen-containing functional groups (C–O and C=O) may participate in the complexation with Cd. respectively, which may be attributed to reactions with soil Cd. Furthermore, the content of M-OH decreased from 29% to 19%, while the content of C-OH increased from 24% to 62% in FeCaBC treatment, which may be attributed to the adsorption reaction between FeCaBC and Cd forming Fe-O-Cd/C-O-Cd complexes.

The environmental stability and carbon sequestration potential of the materials were evaluated by assessing their antioxidant properties through carbon loss after H_2O_2 oxidation (Du et al. 2019). Higher carbon loss indicates lower resistance to H_2O_2 oxidation and poorer chemical stability of the material. As shown in Fig. 4(a), the carbon loss rates of BC, FeBC, CaBC, and FeCaBC were 45%, 21%, 24%, and 18%, respectively. Evidently, FeCaBC exhibited the lowest carbon loss, demonstrating superior stability among all materials.

In the TG curve, mass loss between 200 and 550 °C is attributed to SOC, while mass loss above 550 °C is ascribed to soil inorganic carbon (SIC) and residual substances in the soil (Barros et al. 2011). In this study, the relative mass loss between 200 and 550 °C (attributed to thermal decomposition of organic matter) accounted for 51% of the total mass loss in CK (Fig. 4(b). After adding 2% BC, CaBC, FeBC, and FeCaBC, the relative mass loss rates of SOC in the soil were 45%, 21%, 24%, and 17%, respectively. Undoubtedly, the lowest soil SOC loss was observed with FeCaBC addition, indicating that FeCaBC possesses optimal stability and contributes to increasing soil organic carbon.

3.5 Correlation analysis and structural equation modeling

To further identify the key factors influencing the Cd reduction and CO_2 emissions by remediation materials, a correlation analysis was performed between soil nutrients, DTPA-Cd content, Cd fractions, and CO_2 emissions. As shown in Fig. 5(a), a significant negative correlation was observed between exchangeable Cd and dosage of biochar, incubation time, and the content of CEC, pH value, SOC, available P, and ammonium N in soil ($P<0.05$). Soil CO_2 emissions and EX-Cd were significantly positively correlated with DTPA-Cd content ($P<0.05$).

Using structural equation modeling (SEM), we analyzed the direct and indirect effects of soil physicochemical properties on soil available Cd content and CO_2 emissions. As

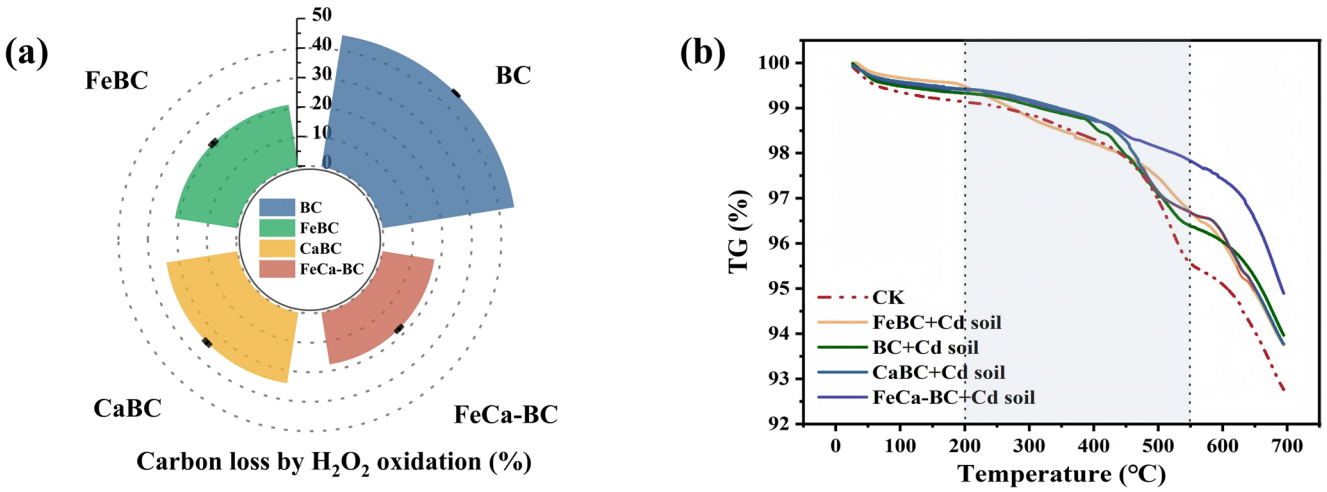

Fig. 4 The carbon loss rate of materials after H_2O_2 oxidation treatment (**a**) and the thermogravimetric (TG) curves of Cd-contaminated soil amended with materials (**b**)

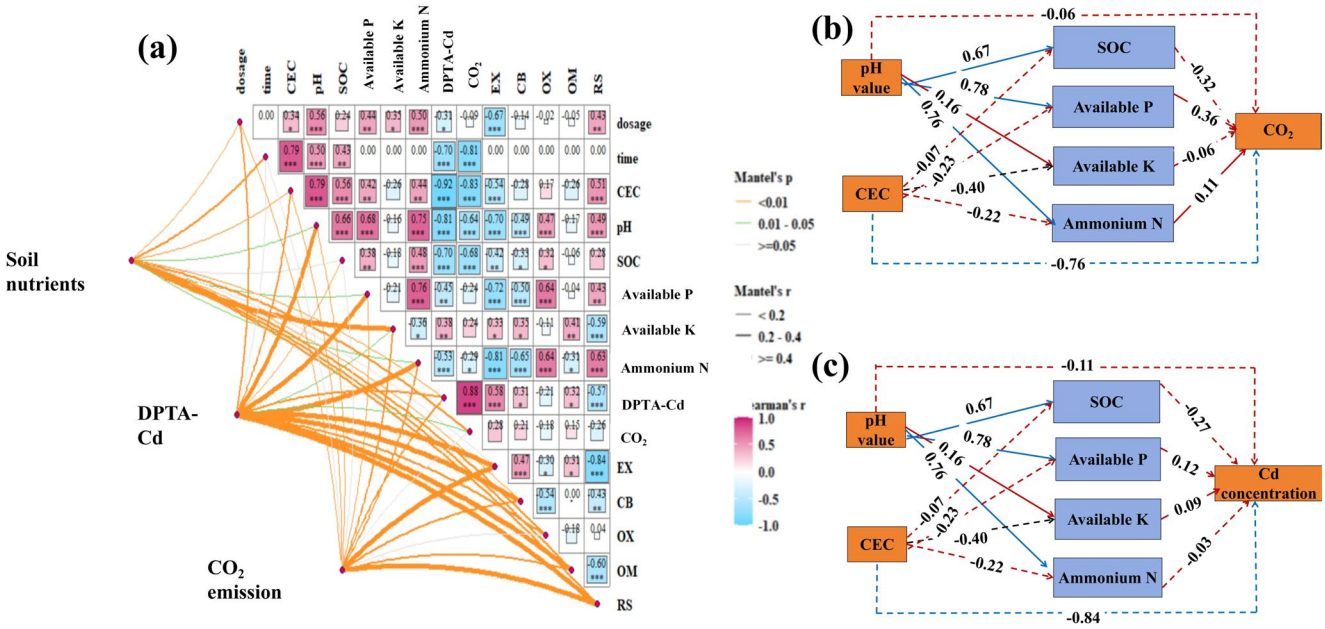

Fig. 5 Correlation between soil nutrients, DPTA-Cd, CO_2 emissions, and Cd fraction (**a**); Structural equation model (SEM) analysis of the effect of remediation materials on soil CO_2 emissions (**b**) and available Cd content (**c**)

shown in Figs. 5(b–c), the content of CEC was directly and negatively correlated with DTPA-Cd and CO_2 emissions ($P<0.05$). And soil pH exerted a significant positive direct effect on SOC, available P, and ammonium N ($P<0.05$). In contrast, SOC, available P, and ammonium N directly affected DTPA-Cd and CO_2 emissions, although the correlations were not significant. This suggests that soil pH value may indirectly influence DTPA-Cd and CO_2 emissions by regulating intermediate variables such as SOC, available P, and ammonium N, thereby further suppressing Cd bioavailability and CO_2 emissions. The SEM results indicate that the pathways of FeCaBC immobilized Cd and reduced CO_2 emissions involve two aspects: (1) a directly effect by increasing soil CEC content; (2) an indirectly effect by altering SOC, available P, and ammonium N contents through soil pH regulation.

4 Discussion

4.1 Effects of FeCaBC on soil physicochemical properties

In this study, soil pH values increased across all amendment treatments. Compared to CK, FeCaBC addition elevated soil pH, potentially due to the hydrolysis of alkaline minerals (including Fe^{3+} and Ca^{2+}) (Guan et al. 2022). Over time, alkaline ions leached from FeCaBC could reduce the concentration of H^+ through adsorption and complexation, thereby increasing soil pH value (Singh et al. 2023). These results are consistent with previous studies, which have demonstrated that biochar treatment shifts acidic soils toward neutrality or alkalinity (Lu et al. 2022).

Soil CEC is a crucial indicator for evaluating soil fertility and buffering capacity (Yu et al. 2024). In this study, CEC contents increased in all treatments with biochar and modified biochar, indicating that the application of these materials can enhance soil nutrient retention and buffering capacities. Among them, soil CEC in the FeCaBC treatment was significantly higher than that in the FeBC and CaBC treatments. This result may be attributed to the presence of Ca^{2+}, Fe^{2+}, and Fe^{3+}, along with abundant oxygen-containing functional groups (e.g., -COOH and -OH) in FeCaBC, which is consistent with previous research findings (Fidel et al. 2017).

FeCaBC improved soil nutrient availability and chemical properties. In this study, FeCaBC addition significantly increased soil contents of available K, available P, and ammonium N, indicating that FeCaBC can improve soil fertility and facilitate the formation and transformation of soil nitrogen (N), phosphorus (P), and potassium (K). Fe is stably loaded on the biochar surface to form Fe-O functional groups that exhibit strong affinity for Cd and realize effective Cd immobilization. Simultaneously, FeCaBC, as a material with high carbon content, stable structure and abundant porous structure, significantly elevates soil organic carbon contents after application, which may further contribute to the increase of soil available P content. The increase in these indicators may be attributed to FeCaBC enhancing soil electrostatic attraction (Yao et al. 2012), promoting

phosphate release and improving phosphorus availability (Oladele et al. 2019), and elevating soil carbon and nitrogen contents (Güereña et al. 2013). Overall, changes in soil physicochemical properties collectively influence soil quality (Han et al. 2024). Among the materials tested, FeCaBC demonstrated the greatest ability to enhance soil nutrient transformation, likely owing to its large specific surface area (141.80 m^2/g), thereby improving nutrient adsorption and retention (Xia et al. 2022).

4.2 Effect of FeCaBC on Cd in soil

Due to the mobility and persistent accumulation of heavy metals, agricultural soils are particularly vulnerable to contamination by heavy metals. Biochar, with its unique physical structure, can adsorb bioavailable Cd in soil, thereby alleviating Cd toxicity to plants. In this study, the addition of FeBC, CaBC, and FeCaBC significantly reduced soil DTPA-Cd content and facilitated the Cd transformation of exchangeable into Fe-Mn oxide-bound and residual fractions, which exhibit less toxicity to crops. Among the four materials, FeCaBC exhibited the best performance in immobilizing soil available Cd. In the pot experiments of this study, application of 0.5%-2% FeCaBC significantly reduced Cd content in ryegrass (by 10%-30%), confirming hypothesis 1 that FeCaBC as an effective material for remediating Cd-contaminated soil.

Biochar indirectly affects the availability of heavy metals in soil by altering soil physicochemical properties, such as soil pH and CEC (Su et al. 2024; Xiang et al. 2024). This study further clarified the regulatory mechanism by which FeCaBC affects soil Cd availability through a combined analysis of correlation heatmaps and SEM. The results show that dosage rate of FeCaBC was positively correlated with soil pH and CEC, and significantly negatively correlated with DTPA-Cd content ($P<0.05$), indicating that FeCaBC can suppress Cd bioavailability. FeCaBC addition also significantly increased soil pH, promoting chemical precipitation reactions between Cd^{2+} and OH^-, facilitating the conversion of available Cd into stable fractions, and reducing Cd bioavailability, thereby achieving immobilization of Cd in soil (Su et al. 2024). Additionally, a significant increase in soil CEC treated by FeCaBC could provide more active sites for Cd adsorption, and may synergistically enhance the stability of mineral-organic matter complexes under alkaline conditions, further reducing the risk of Cd uptake by plants (Wu et al. 2020). Previous studies have shown that increased soil organic carbon and nutrient contents contribute to reducing available Cd content (Bolan et al. 2014). In this study, FeCaBC application significantly increased the contents of SOC, available P, and available K in soil. According to the SEM results, soil pH exerts a direct positive effect on SOC and AP content. Increased SOC and AP can undergo chelation and precipitation with Cd, thus significantly reducing Cd bioavailability (Shahid et al. 2017). Additionally, elevated available K content can facilitate competitive inhibition of Cd uptake by plant roots (Zhao et al. 2019), thereby reducing Cd accumulation in aboveground plant.

In addition to the indirect effects, the direct Cd adsorption of FeCaBC is a key mechanism for reducing soil Cd availability. In our previous studies, owing to the abundant oxygen-containing functional groups and large specific surface area, FeCaBC demonstrated an outstanding Cd adsorption capacity in solution (78.0 mg/g), significantly outperforming other biochars (Xiang et al. 2024) This study further investigated the mechanism by which FeCaBC remediates Cd-contaminated soil through characterization of soils with and without this material. According to FTIR and XPS results, the surface of FeCaBC contains abundant metal-oxygen and other oxygen-containing functional groups, providing numerous adsorption sites for Cd immobilization. The observed abundant -OH, C=O, C-O, Fe-O, and Ca-O groups can undergo complexation and ion exchange reactions with Cd^{2+}, forming complexes such as C-O-Cd (Qu et al. 2021), which is consistent with spectral characterization results (Qu et al. 2021). After 60 days of incubation, soil treated with FeCaBC exhibited significantly higher levels of oxygen-containing functional groups than other treatment groups, indicating that FeCaBC enhances the stabilization of available Cd in soil by increasing active sites on soil particles (Zhu et al. 2022). Additionally, TG analysis revealed that FeCaBC-treated soil had the lowest SOC loss (18%), indicating that FeCaBC application enhances soil organic carbon stability and reduces carbon dioxide release.

In summary, the primary mechanisms by which FeCaBC immobilizes Cd in soil in this study are as follows: (1) Abundant oxygen-containing functional groups (Fe-O, Ca-O, -COOH, -OH) interact with Cd through complexation and ion exchange, thereby reducing Cd bioavailability in soil; (2) Indirectly promoting the transformation of bioavailable Cd into stable fractions by increasing soil pH and CEC; (3) Increased soil nutrient contents (e.g., SOC, available P, and available K) synergistically reduce soil Cd availability and Cd accumulation in organisms through multiple mechanisms, including complexation, precipitation, and ion competition.

4.3 Effects of FeCaBC on soil organic carbon and CO_2 emissions

Previous studies have demonstrated that the application of biochar enhances soil carbon and reduce CO_2 emissions (Joshi et al. 2022). Regarding hypothesis 2 in this study, the

results indicate that the application of BC, FeBC, CaBC, and FeCaBC effectively increased soil SOC content, with FeCaBC exhibiting the most significant highest increase (130%-134%), exceeding the previously reported range of 50% to 120% in the literatures (Cheng et al. 2024; Yang et al. 2022). The increase in soil SOC may be attributed to FeCaBC, as a carbon-rich material, introduces a large amount of stable carbon into the soil over a short period while simultaneously inhibiting the mineralization of readily organic carbon(Yang et al. 2022). Based on the C content of the materials listed in Table S1, the direct carbon input resulting of 0.5%-2% FeCaBC application ranges from 2.51 to 10.04 g C/kg, further supporting these results.

However, soil CO_2 emissions showed a downward trend compared to the CK following the application of FeCaBC, primarily due to its unique structural characteristics and its impact on the soil environment(Wang et al. 2025b). Characterization results from FTIR and XPS indicated that the surface chemical properties of FeCaBC underwent significant changes compared to BC, with a notable increase in the content of functional groups such as C-O and C=C. These groups could stabilize labile small organic molecules in soil, promote their polymerization and transformation, and effectively inhibit the decomposition and release of labile carbon, and ultimately reduce CO_2 emissions (Ji et al. 2024; Liang et al. 2010). More importantly, the synergistic effect of loaded iron/calcium on FeCaBC enhances the chemical bonding capacity of functional groups such as C-O/C=C, further improving the chemical sequestration efficiency of organic carbon (Bao et al. 2022; Chen et al. 2020). Additionally, the interaction between exogenous minerals introduced by the modifier and biochar enhances the chemical antioxidant properties and thermal stability of FeCaBC (Fig. 4), delaying the carbon decomposition process. This increases soil SOC content and reduces CO_2 emissions, indicating potential for short-term carbon retention under the present experimental conditions (Xu et al. 2021; Yang et al. 2018).

The changes of soil CO_2 emissions were analyzed by FTIR characterization, TG carbon loss and CO_2 emission data. The FTIR spectra of FeCaBC-amended soil showed a significant enhancement of Ca-O vibration peaks at 698 cm^{-1} and carbonate functional group signals at 1452 cm^{-1}, confirming the formation of stable $CaCO_3$ in soil. This result is consistent with the finding that alkaline metal-doped biochar can react with CO_2 to form carbonate minerals (Othman et al. 2021). Meanwhile, the intense -OH, C-O and C=C peaks indicated the enrichment of stable organic carbon, in line with the observation that Fe-modified biochar promotes the polymerization of soil organic molecules (Wang et al. 2023b). TG analysis indicates that soil organic carbon (SOC) is the primary factor causing mass loss within the 200–550 °C, while inorganic carbon ($CaCO_3$) remains stable above 550 °C without obvious weight loss (Barros et al. 2011). In this study, the temperature range with the lowest SOC loss (17%) in FeCaBC-treated soil coincided with the maximum reduction in CO_2 emissions (30%-37%), demonstrating that soil CO_2 emissions were predominantly derived from SOC mineralization rather than $CaCO_3$ decomposition. This result is supported by previous research that mineral-enriched biochar primarily reduces organic carbon-derived CO_2 emissions (Buss et al. 2022). The carbon balance demonstrates that FeCaBC significantly increased SOC stock and mitigated CO_2 emission by stabilizing organic carbon and forming stable inorganic carbonates.

In addition, the enhanced oxygen-containing functional groups (Fe-O, Ca-O, C-O) in FTIR spectra not only improved the sequestration of organic carbon but also inhibited the microbial mineralization of labile organic carbon, thus synergistically reducing CO2 emissions from organic carbon breakdown, which is consistent with the mechanism that functional group-rich biochar suppresses carbon decomposition by stabilizing soil organic matter.

The mechanism by which soil pH affects CO_2 emissions exhibits significant multidimensional characteristics. Traditional theory holds that microbial activity is inhibited in acidic soil environments (pH<5.5), which can reduce the mineralization of soil organic matter and CO_2 emissions (Rousk et al. 2010). However, the results of this study indicate that soil pH and organic carbon content increased by 4%-8% and 130%-134%, respectively, while CO_2 emissions decreased by 30%-37% after FeCaBC application. This result may be attributed to alkaline conditions promoting the formation of organic-mineral complexes, and enhancing the protection of organic carbon(Choudhary et al. 2025). Additionally, the soil pH value in this study is conducive to the preservation of inorganic carbon, as a significant increase in the proportion of bicarbonate when pH>7, whereas inorganic carbon is more likely to precipitate as insoluble carbonate minerals at lower pH levels (Pratt et al. 2025). Furthermore, slightly elevated soil pH in the FeCaBC treatment could improve microbial efficiency in carbon utilization, accelerate biological carbon sequestration, and increase organic carbon content while reducing CO_2 emissions (Pei et al. 2021).

Soil CEC also regulates CO_2 emissions, with its mechanism influenced by soil mineral composition and organic carbon forms. Application of FeCaBC significantly increased soil CEC values (with the maximum increase of 113%), and this change suppressed CO_2 emissions through two pathways. On the one hand, improved CEC could enhance the soil capacity to adsorb and immobilize organic matter, thereby reducing the accessibility of organic carbon to decomposition (Domeignoz-Horta et al. 2020). On the other hand, the soil exhibits synergistic enhancement of

carbon pool stability through chemical and biological processes under the conditions of high CEC and high pH in FeCaBC treatment, thereby reducing CO_2 emissions (Singh et al. 2021).

In summary, the primary mechanisms of FeCaBC in Cd immobilization in soil are as follows: (1) Abundant oxygen-containing functional groups (Fe-O, Ca-O, -COOH, -OH) interact with Cd through complexation and ion exchange, thereby reducing Cd bioavailability in soil; (2) Indirectly promoting the transformation of bioavailable Cd into stable fractions by increasing soil pH and CEC; (3) Increased soil nutrient contents synergistically reduce soil Cd availability and Cd accumulation in organisms through multiple plausible mechanisms, including complexation, precipitation, and ion competition.

4.4 Practical implications and limitations

Although FeCaBC exhibited effective Cd passivation and carbon sequestration at 0.5–2% (w/w) in this study, its practical applications remain limited. The results of this work were based on artificial cadmium contaminated soil of 30-day aging, which differs significantly from natural field soils where long-term Cd aging, ion competition for adsorption sites and dynamic redox changes may alter FeCaBC's performance. In addition, the leachability and long-term release behavior of Fe/Ca-associated components were not directly evaluated in this study and should be assessed in future work before large-scale field application. Furthermore, the large-scale application of FeCaBC may be constrained by cost factors. Notably, under identical application conditions, FeCaBC demonstrated significantly higher Cd immobilization efficiency (37%-52%) compared to other amendments, such as Fe-Zn-modified biochar (15–30%) (Yang et al. 2025) and manganese-modified biochar (25–40%) (Su et al. 2025). The following research should be conducted to explore low-cost raw biomass and combination with inexpensive modifiers, optimize the minimum effective dose of FeCaBC to reduce costs, and validating practical efficacy through long-term field trials.

5 Conclusion

This study investigated the effects and underlying mechanisms of FeCaBC application on nutrient availability, Cd immobilization, and CO_2 emissions in Cd-contaminated soil. The results demonstrate that FeCaBC increased soil pH and CEC, while enhancing the content of available nutrients (available K, available P). Application of 0.5%-2% FeCaBC significantly reduced the DTPA-Cd content in soil (37%-52%), increased soil organic carbon content (130%-134%), reduced soil CO_2 emissions (30%-37%), and inhibited Cd accumulation in ryegrass (10%-31%). SEM analysis indicated that adding FeCaBC directly and indirectly reduced soil available Cd content and CO_2 emissions by influencing soil pH and CEC. The results of FTIR and XPS analyses indicate that FeCaBC facilitates Cd fixation, organic carbon stabilization, and CO_2 mitigation through complexation and precipitation mechanisms mediated by its oxygen-containing functional groups (C-O, Fe-O, and Ca-O). This study characterizes calcium-iron composite modified biochar for dual effects of Cd passivation and carbon sequestration in heavy metal-contaminated soil.

Glossary

BC	Biochar
CB	Carbonate-bound fraction
DTPA	Diethylenetriaminepentaacetic acid
EX	Exchangeablefraction
FeCaBC	Fe-Ca composite modified biochar
FTIR	Fourier-transform infrared spectrometer
OM	Organic matter-bound fraction
OX	Fe-Mn oxide bound fraction
RS	Residual fraction
SEM	Structural equation model
XPS	X-ray photoelectron spectroscopy

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Data availability Data will be made available on request.

Declarations

Competing interests Authors declare no competing interests.

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