

RESEARCH ARTICLE

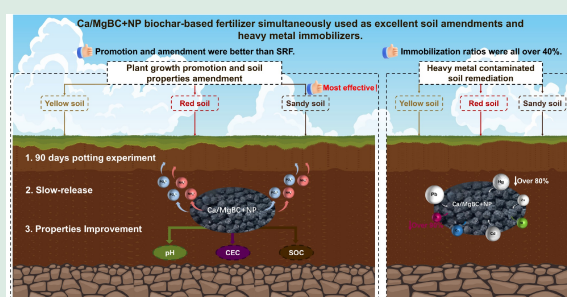
Struvite-loaded biochar beads fertilizer for different soils: nutrient slow release, soil properties improvement and heavy metal remediation

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HIGHLIGHTS

- Ca/MgBC + NP showed satisfactory slow-release properties in various soils.
- Ca/MgBC + NP effectively promoted crop growth in various soil types and pH levels.
- Ca/MgBC + NP improved soil properties in a variety of soil types and pH levels.
- Ca/MgBC + NP effectively immobilized heavy metals, particularly Cr and Hg (over 80%).



ABSTRACT: This study investigates the use of struviterient-loaded magnesium-modified biochar beads (Ca/MgBC + NP) as a slow-release fertilizer and soil amendment, comparing its performance with commercially available slow-release fertilizers (SRF) in different soils and crop types. The results demonstrate that Ca/MgBC + NP exhibited satisfying swelling, water retention, and slow-release properties in all tested soils. In sandy soil, which showed the most significant differences ($p < 0.05$), Ca/MgBC + NP enhanced the growth of *Brassica chinensis* L. and *Spinacia oleracea* L. after 90 d, with shoot and root lengths, as well as fresh and dry weights, 1.25–2.84 times higher than those treated with SRF. The cation exchange capacity and organic carbon content of sandy soil were significantly improved (by 38.55% and 265.38%), overcoming its natural limitations in water and fertilizer retention. Principal Component Analysis (PCA) confirmed that soil properties played a crucial role in crop growth (52.67% variance explained). Spectroscopic analysis indicated that magnesium-related compounds, including struvite and $\text{Mg}(\text{PO}_4)_3$, contributed to the observed growth promotion. Furthermore, Ca/MgBC + NP effectively immobilized heavy metals, particularly Cr and Hg, with immobilization rates exceeding 80%. This study highlights the potential of Ca/MgBC + NP as a sustainable, low-cost fertilizer that not only enhances crop growth but also improves soil health and remediates heavy metal contamination, providing a promising alternative for green agriculture.

KEYWORDS: Sustainable development, Slow-release fertilizer, Release behavior, Pot experiment, Soil property improvement, Heavy metal remediation

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1 Introduction

Agricultural production provides food, energy, and other important security for a rapidly growing population (Dou et al., 2023). Fertilizer application is vital for agricultural production to improve soil fertility and increase food crops per unit area (Xiao et al., 2022; Wang et al., 2024a). Among them, phosphorus fertilizer and nitrogen fertilizer are the two types of fertilizers in high demand by plants. Urea (Antor et al., 2023), as the common nitrogen fertilizer, despite its advantages of high nitrogen content (46% N), good water solubility, and low cost, suffers from high loss rates due to leaching and volatilization, which not only affects crop yields but also contributes to agricultural environmental pollution (Kottegoda et al., 2017; Lu et al., 2022). Common phosphorus fertilizers (calcium phosphate, diammonium phosphate, potassium dihydrogen phosphate) also face problems of high prices and causing soil degradation (Zhuang et al., 2024; Gong et al., 2025; Zhang et al., 2025b). To improve the efficiency of nutrient use while mitigating environmental pollution, and developing green and sustainable agriculture, slow-release fertilizers have been widely produced (Yesigat et al., 2022; Duan et al., 2023; Luo et al., 2024). Slow-release fertilizers significantly reduce possible nutrient losses between fertilizer application and plant uptake through gradual release of nutrients (Liu et al., 2020), as well as volatilization losses of ammonia (Xiao et al., 2021), significantly reducing environmental pollution.

The diversity in the properties and structure of biochar (BC) has given it the potential to be used in several fields (Wang et al., 2024b; Yadav et al., 2024). To date, the application of BC in environmental remediation (Jin et al., 2018; Zhong et al., 2019; Li et al., 2024a; Zhang et al., 2024), agriculture (Karim et al., 2019), and carbon sequestration (Carneiro et al., 2018; Xiao et al., 2018) has already attracted the attention of many researchers. For agriculture, biochar, as a porous carbon-containing material rich in multiple functional groups, contributes to the retention of nutrients and water in the soil when used directly in agriculture (Wu et al., 2019b; Xia et al., 2020; Fachini et al., 2022). Using biochar as a carrier (Chen et al., 2018; Xia et al., 2020), synthetic biochar-based slow-release fertilizers could achieve slow release of nutrients and promote plant growth (Chen et al., 2017; Hagemann et al., 2017). For example, phosphorus-loaded biochar-based fertilizers synthesized by copyrolysis of cotton straw with H_3PO_4 by An et al. (An et al., 2021) showed excellent slow-release properties.

Slow-release fertilizers prepared from KH_2PO_4 -IA-modified cotton stalks biochar by Shang et al. (2022) showed good water absorption, water retention, and slow-release properties, and had the potential to promote the growth of cucumber seedlings. Lu et al. (2023) incorporated hydrotalcite and starch into the biochar-based fertilizer, the composite slow-release fertilizer obtained improved the water retention performance of the soil and the nutrient utilization rate of the plant, and promoted the growth of tomato plants. Based on the good performance of biochar itself, and then through the modified treatment of biochar, which has a significant role in promoting the water retention performance of the soil, the fertility of the fertilizers, and the growth of plants.

In addition, the electronegativity, alkalinity, and rich functional groups of biochar make it change the physicochemical properties of soil during application (Li et al., 2023d; Singh et al., 2023). For example, Yuan et al. (2023) concluded that biochar was effective in improving the physicochemical properties and biological health of salt-affected soils. Li et al. (2023c) demonstrated that biochar was more effective than liming in improving soil properties under acid rain conditions. Meanwhile, the quality of the soil environment in China is not optimistic, heavy metal contamination is prominent (Liu et al., 2023; Yang et al., 2023). Heavy metal pollutants in soil mainly include chromium, mercury, lead, cadmium, copper, zinc, and nickel. The remediation of soil on agricultural land is different from common contaminated soil because of the need to undertake production functions. The use of biochar for remediation of soil heavy metal contamination could be both cost-effective and environmentally beneficial (Li et al., 2024b). For example, Li et al. (2020) prepared biochar loaded with nano zero-valent iron, which achieved 66% immobilization of Pb under acid rain conditions. The iron sulfur modified biochar prepared by Wu et al. (2019a) effectively reduced the concentration of exchangeable Cd in soil (18.53%). The modified natural diatomite using acid treatment and ultrasonic treatment by Ye et al. (2015) reduced the concentration of Pb, Cu, and Cd (66.7%, 47.2%, and 33.1%) in simulated soil. It is evident that there is considerable research on biochar remediation of contaminated soil, and studies on biochar-based fertilizers are more focused on crop yield enhancement, while less research has been focused on the effect of biochar-based fertilizers on different kinds of soils and plants, the ability of planting soil improvement and the potential of heavy metal soils remediation. Li et al. (2024b) developed a zeolite/biochar composite for soil quality

improvement and remediation of Pb^{2+} and Cd^{2+} heavy metals in stems (92.8% and 92.9%)

Our previous studies have shown that Ca/MgBC obtained by Mg modification-gel-calcination using corn stover as feedstock was able to adsorb both PO_4^{3-} -P and NH_4^+ -N, the adsorbed Ca/MgBC + NP had desirable nutrient retardation behavior and heavy metal adsorption potential in aqueous solution (Li et al., 2023a). It was observed that Ca/MgBC + NP had magnesium ammonium phosphate crystals (struvite) on the surface. Struvite is a multielement compound fertilizer containing nitrogen (N), phosphorus (P) and magnesium (Mg). All of these components are effective for plant growth and slowly decompose when applied to the soil, providing plants with readily available nutrients (Gao et al., 2024).

Therefore, in this study, the adsorbed Ca/MgBC + NP was further applied to agriculture to investigate the potential application of Ca/MgBC + NP in real soil environments. To ensure that the results are more convincing, three soils with different textures and pH were selected in this study, the swelling behavior, water retention and slow-release properties of Ca/MgBC + NP in different soils, compared with commercially available slow-release fertilizers (SRFs) were investigated. Based on this, phosphorus-loving *Brassica chinensis* L. and nitrogen-loving *Spinacia oleracea* L. were selected to explore the effects of different forms of Ca/MgBC + NP and SRF on plant growth through pot experiments. Finally, the property improvement of Ca/MgBC + NP on planting soil and the remediation of heavy metal polluted soil were examined via soil column leaching experiments. This study aims to achieve an effective combination of soil fertility enhancement, crop growth promotion, soil quality improvement, and soil contamination remediation by systematically investigating the effects of our Ca/MgBC + NP on different types of soils and crops.

2 Materials and methods

2.1 Materials

The methods and materials used to prepare Ca/MgBC + NP were referred to our previous work (Fig. S1) (Li et al., 2023a). Among them, Ca/MgBC + NP in powder form denoted as Ca/MgBC + NP(p), while Ca/MgBC + NP(b) was represented in bead form, and if not otherwise stated Ca/MgBC + NP was also represented in bead form. According to the national standard GB/T 17767-2010 ‘Determination of Compound Fertilizers’

(Part 1: Total nitrogen content and Part 2: Total phosphorus content), after testing and calculations, the N and P contents of Ca/MgBC + NP were both 7.68%.

The slow-release fertilizer (SRF) was purchased from Dezhou Xiaoyuan Landscaping Co., Ltd., China, and the nitrogen and phosphorus contents were both 14%. For crops, we chose *Brassica chinensis* L., which is sensitive to phosphorus fertilizer, and *Spinacia oleracea* L., which is sensitive to nitrogen fertilizer. Seeds of both crops were purchased from Hejin Agricultural Science and Technology Hebei Co., Ltd., China.

Based on the representation of soil types and the diversity of soil properties, soils with different textures (sandy and clay soil) and pH were selected for this study. Specifically, yellow soil is a typical alkaline clay soil, sandy soil is a typical alkaline sandy soil, and red soil is an acidic clay soil. In addition, yellow soils are widely distributed in temperate and semi-arid regions, sandy soils are widely distributed in desert fringe areas, arid and semi-arid regions, and red soils are mainly distributed in tropical and subtropical regions. In summary, the selection of yellow soils, red soils and sandy soils as research objects is not only representative and diverse, but also the results of their research are widely applicable on a global scale. The yellow soil, red soil, and sandy soil were obtained from Zhejiang, Henan, and Sichuan of China. The soil samples were sterilized at high temperature and then blown dry at room temperature and sieved through a 10-mesh sieve, their physicochemical properties were shown in Table 1. All chemical reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water (DI, PLUS-E2R20UV, EPED, China) was used for all experiments.

2.2 Swelling and water retention capacities experiment

We comparatively analyzed the swelling and water retention capacities of Ca/MgBC + NP and SRF. To analyze the swelling capacity of Ca/MgBC + NP in detail, we studied both Ca/MgBC + NP(b) and Ca/MgBC + NP(p), in addition to this property of original biochar powder (BC), magnesium-modified biochar powder (MgBC), and magnesium-modified biochar beads (Ca/MgBC), and two parallel sets of experiments. The procedures for determining the swelling capacities of samples were as follows: 0.1 g of each dried sample was wrapped in a 200-mesh nylon bag at room temperature, and weighed as M_0 . The nylon bags with different samples were entered into DI and soaked until saturated (about 12 h). The swollen

Table 1 Basic physical and chemical properties of soil samples

Soil	pH	Available phosphorus (AP) (mg/kg)	Ammonia nitrogen (NH ₄ ⁺ -N) (mg/kg)	Soil organic carbon (SOC) (mg/kg)	Cation exchange capacity (CEC) (cmol/kg)
Yellow	8.0	54	0.67	1.8	9.6
Red	5.5	54	0.72	1.2	7.9
Sandy	8.1	54	1.23	2.6	8.3

Notes: Available phosphorus (AP): a general term for the phosphorus in the soil that can be absorbed and utilized by plants. Soil organic carbon (SOC): the sum of the carbonaceous organic matter in the soil. Cation exchange capacity (CEC): the total amount of various cations that can be adsorbed by soil colloids.

samples were filtered to remove free water and weighed (M_1), the swelling capacity (Q_{eq}) was calculated according to Eq. (1) (Cheng et al., 2020):

$$Q_{eq} = \frac{M_1 - M_0}{M_0} \tag{1}$$

The water retention capacities of the samples were further investigated as follows: 1.0 g of each dried sample was mixed well with 150 g of dried soil, and packed in a jar (W_0), poured into 50 mL DI to saturate the soil (W_1), left at room temperature for 29 d and weighed at regular intervals (W_t). The water retention ratio (WR%) was calculated by the Eq. (2) (Sui et al., 2021).

$$WR\% = \left(\frac{W_t - W_0}{W_1 - W_0} \right) \times 100\% \tag{2}$$

2.3 Slow-release behaviors in soil

To investigate the slow-release behavior of Ca/MgBC + NP in soil, we conducted slow-release experiments in all three soils, with SRF as the control, two parallel sets of experiments. The nutrient release behavior of the samples in soil was investigated by performing the indoor simulated soil column leaching experiment. The

soil column was made of a chromatography column with an inner diameter of 3 cm and a height of 30 cm (Fig. 1(a)), and the specific design scheme was shown in Text S1.

The frequency of experimental water addition was calculated based on the average daily precipitation in Xi'an in the last ten years (Text S2 & Table S1). In the simulated soil column leaching experiment, two groups of treatments were set up (Ca/MgBC + NP and SRF), each with three replicates. The release amounts of N and P were determined by collecting the bottom drench solution at different release times (1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30 d). The kinetic analysis of the slow-release behavior of P and N in Ca/MgBC + NP in three soils was performed by fitting the data (Zero-order (Eq. (3)), First-order (Eq. (4)), Higuchi (Eq. (5)), Hixson-Crowell (Eq. (6)) and Baker-Lonsdale (Eq. (7)) models) (Costa and Sousa Lobo, 2001; Ye et al., 2020).

$$\frac{M_t}{M_\infty} = k_0 t, \tag{3}$$

$$\ln \left(1 - \frac{M_t}{M_\infty} \right) = -k_1 t, \tag{4}$$

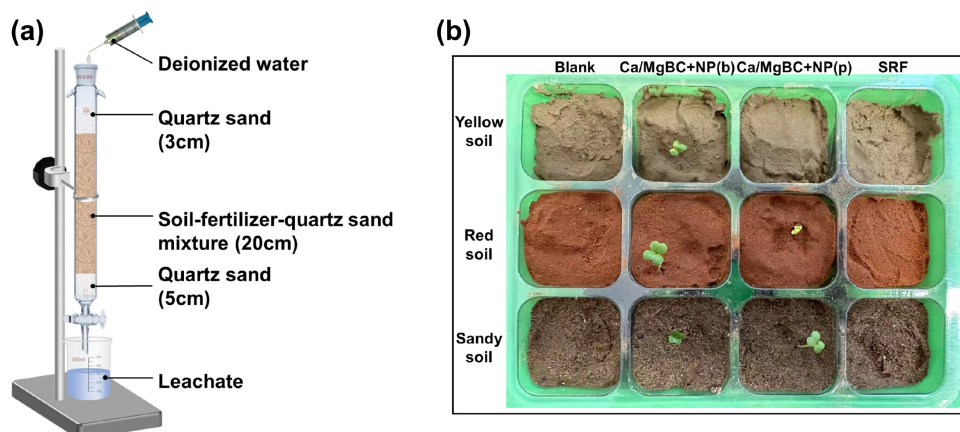


Fig. 1 (a) Schematic figure of the leaching experiment; (b) schematic photographs of the seedling experiment (from top to bottom, each row shows yellow soil, red soil and sandy soil, experiments were replicated three times).

$$\frac{M_t}{M_\infty} = k_2 t^{\frac{1}{2}}, \quad (5)$$

$$\left(1 - \frac{M_t}{M_\infty}\right)^{\frac{1}{3}} = 1 - k_3 t, \quad (6)$$

$$\frac{3}{2} \left[1 - \left(1 - \frac{M_t}{M_\infty}\right)^{\frac{2}{3}}\right] - \frac{M_t}{M_\infty} = k_4 t, \quad (7)$$

where M_t/M_∞ is the release ratio of P or N in different time intervals, k_0 , k_1 , k_2 , k_3 , and k_4 are the release rate constants which were calculated by the five models. The zero-order and the first-order kinetic models were fitted using the linear fit, and the Higuchi, Hixson-Crowell, and Baker-Lonsdale models were fitted using the nonlinear fit, and the release rate constants k was obtained by least squares for all five models.

2.4 Pot experiments

The pot experiment was a three-factor randomized block design. The three factors were type of fertilizer applied, soil type and crop type, with four levels for type of fertilizer applied, three levels for soil type, and two levels for crop type (Table S2). In total, there were 24 treatments (2 crops \times 3 soils \times 4 fertilizers), which means that there were 72 plots (24 treatments \times 3 replications) in our study.

Ca/MgBC + NP(b) and Ca/MgBC + NP(p) were studied to investigate the effect of fertilizer form and the rate of powder mass transfer. The experiment was conducted using seedling (Fig. 1(b)) followed by transplanting method (Fig. S2). Equal amounts of crop seeds were sown in seedling pots containing equal amounts of each of the three types of soil, all of which germinated and were transplanted into transparent plastic pots. Each transparent plastic pot (outer diameter 11.0 cm, height 13.0 cm) was filled with 600 g of soil and compacted. Crops were grown in the transparent plastic pots for 90 d. Relevant developmental parameters were recorded during and at the end of development. Fertilizer was applied with reference to the nutrient demand characteristics of *Brassica chinensis* L. and *Spinacia oleracea* L. respectively, ensuring that the nitrogen and phosphorus content of the fertilizer used in each experimental group was the same, and the specific amount of fertilizer added was determined as follows:

As the prepared and commercially available fertilizers contain both N and P nutrients, nitrogen is the macronutrient (main nutrient) of plants, so the quality of the required fertilizer would be set as the reference amount of N, in accordance with the nitrogen content of

Brassica chinensis L. 0.138 g/(50 g *Brassica chinensis* L.) as well as *Spinacia oleracea* L. nitrogen content of 0.203 g/(50 g *Spinacia oleracea* L.). The calculated fertilizer additions per soil pot are shown in Table S3. To avoid the surface runoff, nutrients deficiencies in the later stages of the crops, fixation of phosphorus by the soil, and volatilization of NH_3 (Xiao et al., 2021), deep application was used for fertilizer application process (fertilizers were applied as deep as possible into the soil, about 10 cm from the crop seed).

2.5 Heavy metal immobilization experiment in soil

Cd, Hg, Cu, Pb, Cr, Zn, and Ni are common heavy metal pollutants in soil. We further investigated the removal of these seven heavy metals from soil by adding Ca/MgBC + NP and set up the blank experiment. The removal of heavy metals from soil by Ca/MgBC + NP was investigated by heavy metal solution leaching experiments. 20 g of soil was dried and filtered into a glass tube, after laying a layer of 200 mesh nylon mesh, a homogeneous mixture of 10 g of soil and 0.5 g of Ca/MgBC + NP was added. Finally, added 5 mg of a homogeneous mixture of $\text{Cd}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$. The leachate was collected continuously by dripping DI from the top of the glass tube for leaching, and then tested the content of heavy metals therein in the leaching solution after 24 h. The heavy metals immobilization ratio in soil was calculated by the following equation (Eq. (8)):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (8)$$

where η (%) is heavy metals immobilization ratio, C_0 (mg/L) and C_t (mg/L) are the leached mass concentrations of heavy metals before and after 24 h of immobilization.

2.6 Experimental measurement methods and microstructural characterization

Soil chemical properties were analyzed following the *Technical Specification for Soil Analysis* (Sen and Gao, 2006). Soil pH was measured using a pH meter (PHB-4, Shanghai INASE Scientific Instrument Co., Ltd., Shanghai, China) (soil-water ratio of 1:10). Available phosphorus (AP) was determined using the sodium bicarbonate extraction method coupled with the Mo-Sb colorimetric technique. Soil organic carbon (SOC) was analyzed via the potassium dichromate oxidation-spectrophotometry method. Both AP and SOC measurements utilized a UV-vis spectrophotometer

(UV-vis, DR6000, HACH, China). Soil ammonia nitrogen was assessed by potassium chloride extraction followed by spectrophotometry using a UV-vis spectrophotometer (TU-1810, PUXI, China). The cation exchange capacity (CEC) was determined according to the *Determination of Cation Exchange Capacity of Forest Soil Standard* (LY/T 1243-1999). Concentrations of Cd, Cu, Pb, Cr, Zn, and Ni in the leachate were analyzed with inductively coupled plasma mass spectrometry (NexION 350D ICP-MS, Perkin Elmer, China), while Hg concentrations were measured using atomic fluorescence spectrometry (AFS-9600, Beijing Haiguang Instrument Co., Ltd., China).

The phase composition of the beads, both before and after the pot experiment, was analyzed using an X-ray diffractometer (XRD-6100, Shimadzu, Japan) with Cu/K α radiation ($k = 1.5418 \text{ \AA}$). Additionally, X-ray photoelectron spectroscopy (XPS, ESCALAB Xi + , Thermo Fisher, USA) was employed to determine the electron binding energies of the beads before and after the slow-release experiment to elucidate the mechanisms of slow-release.

2.7 Statistical analysis

Data in all figures and tables are expressed as mean \pm standard error (SE) based on three replicates ($n = 3$). Statistical analyses were performed using SPSS 27.0 software. Two-way analysis of variance (ANOVA) was applied to evaluate the impacts of soil, fertilizer, and their interactions on plant growth parameters at a significance level of $p < 0.05$. Tukey's HSD test was conducted to analyze the effects of different soil types, fertilizer treatments, and their interactions on these parameters at $p < 0.05$. In the figures and tables,

lowercase letters denote significant differences among treatments at $p < 0.05$, with distinct letters indicating significant differences and identical letters signifying non-significant differences. All figures were created using OriginPro 2018.

3 Results and discussion

3.1 Water retention and swelling capacities

The water absorption and water retention capacities of fertilizers are important indicators for evaluating their practical application potential (Shen et al., 2021). Fertilizers swell in volume when absorb amount of solution, the swelling capacity (Q_{eq}) is commonly used to evaluate the water absorption performance of fertilizers. The results showed that the hydrophobicity of the original BC (Mao et al., 2019) resulted in low water absorption performance of BC (Fig. 2(a)). Due to the presence of hydrophilic MgO and CaCO₃ in MgBC and Ca/MgBC, all Mg-modified biochar samples (MgBC, Ca/MgBC, and Ca/MgBC + NP) had a higher Q_{eq} than BC. More importantly, our Ca/MgBC + NP had higher water absorption capacities than commercially available SRF (nearly 2-fold).

The excellent water retention capacity is important for plant growth during reduced irrigation frequency and drought (Lu et al., 2023). We further compared the water retention performance of Ca/MgBC + NP and SRF (Fig. 2(b)), the water retention capacities of all three soils with the addition of Ca/MgBC + NP were all higher than those of soils with the addition of SRF. The water retention capacity of the clay soil was much better than that of the sandy soil, which is consistent with our study. In summary, Ca/MgBC + NP

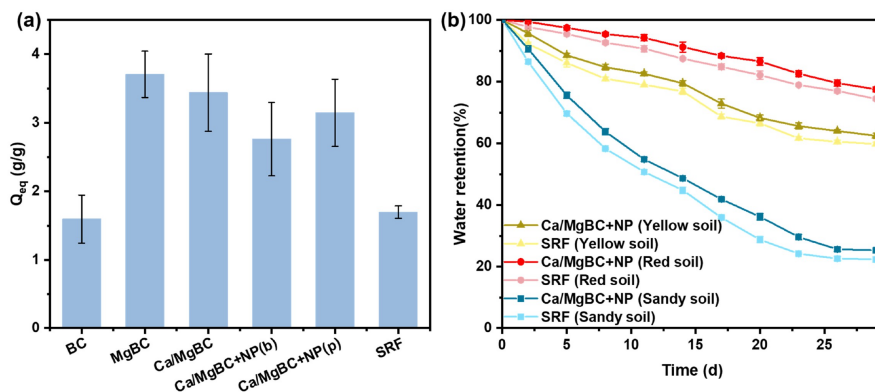


Fig. 2 (a) The swelling capacities of different samples; (b) the water retention capabilities of three kinds of soils with the addition of Ca/MgBC + NP and SRF. Reaction time: 12 h for swelling capacities experiment, 29 d for water retention experiment.

overcomes the inherent hydrophobicity of biochar and has good water absorption and water retention capacities. In addition to absorbing and storing water under water-sufficient conditions, our Ca/MgBC + NP is expected to enhance crop drought resistance and alleviate soil water shortage when water supply is insufficient.

3.2 Sustained release behaviors of Ca/MgBC + NP

3.2.1 Slow-release behaviors

The slow-release behavior of fertilizers in soil is also one of the important indicators to evaluate their application potential (Shang et al., 2022). In previous studies, we have demonstrated that Ca/MgBC + NP had excellent N and P slow-release behaviors in water of different pH (Li et al., 2023a). Through 30-d soil column leaching experiments (Figs. 3(a) & 3(b)), compared with the slow-release behavior of SRF in the three soils, the release of P from Ca/MgBC + NP was

slightly slower than that of SRF, but the release of N was much better, and the deviation of single release of both N and P was smaller. It can be seen that Ca/MgBC + NP was able to release nitrogen and phosphorus stably and uniformly in all three soils, and the release of nutrients was relatively satisfactory.

Ca/MgBC + NP had long sustained slow-release properties in the three soils, the cumulative release ratio of P and N in 24 h were 3.47% and 7.98% (yellow soil), 4.93% and 10.02% (red soil), 6.04% and 14.75% (sandy soil), respectively. 54.60% and 56.38% (yellow soil), 74.87% and 74.06% (red soil), 73.51% and 73.98% (sandy soil) within 28 d, which are in line with the international standards (European Committee for Standardisation) ((1) the release ratio of nutrients is not higher than 15% within 24 h; (2) not higher than 75% in 28 d; (3) the whole release period is not lower than 75%) (An et al., 2020). The excellent permeability of sandy soil resulted in faster nutrient release, for clay soil, nutrients were released more rapidly from acidic red soil than alkaline yellow soil, which was consistent with the results of our study of nutrient leaching

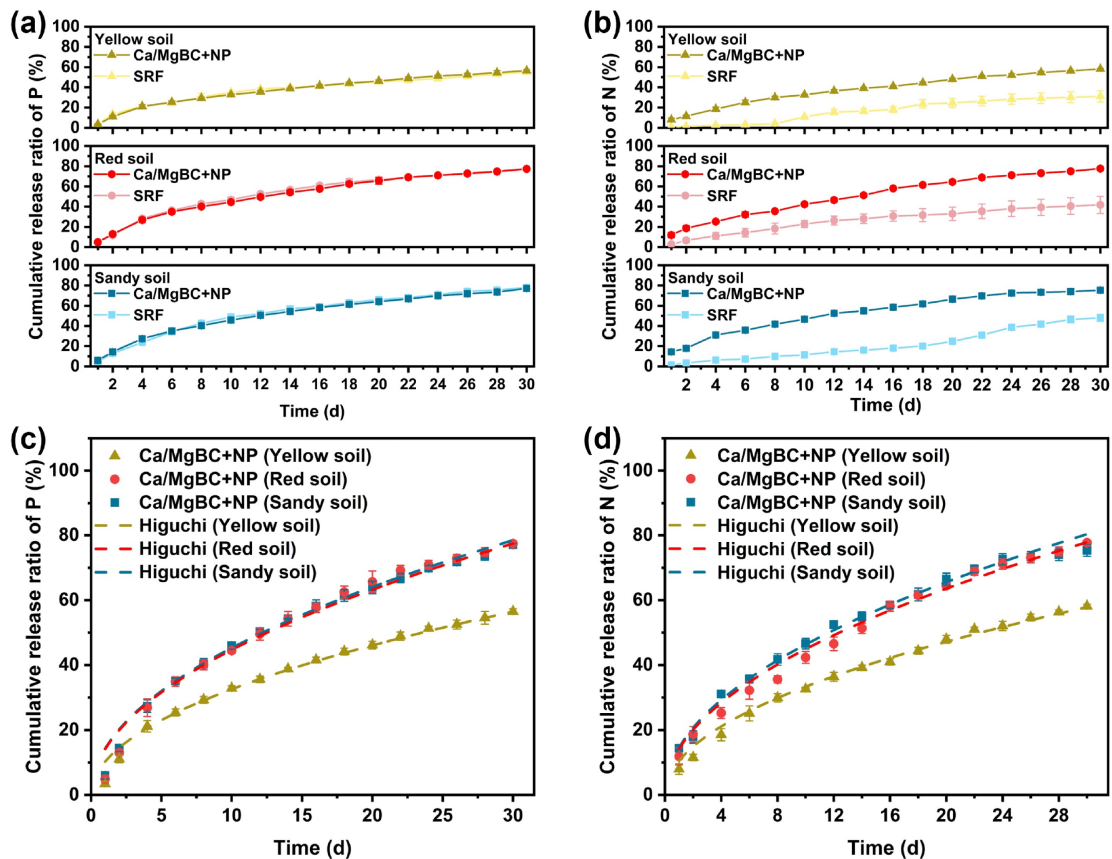


Fig. 3 Cumulative release ratio of (a) P and (b) N from Ca/MgBC + NP and SRF in the three soil; release kinetics of (c) P and (d) N from Ca/MgBC + NP in three types of soil. Reaction time: 29 d.

experiment in water. Therefore, our Ca/MgBC + NP has the potential to be an excellent slow-release fertilizer with stable, long-lasting, and uniform N and P release in soil of different textures and different pH.

3.2.2 Slow-release kinetics

The slow-release kinetics and mechanism of Ca/MgBC + NP in the three soil were further investigated using five models (including zero-order kinetics, first-order kinetics, Higuchi model, Hixson-Crowell model and Baker-Lonsdale model) as shown in Table 2. For the three soils, the Higuchi model fitted the P and N release data better than the other models (R^2 closest to 1, and $R^2 > 0.95$ for both plants in all three soils), suggesting that the release of P and N from Ca/MgBC + NP should be mainly dependent on the diffusion mechanism (Siepmann and Peppas, 2011), the fitted lines of P and N releases modeled by the Higuchi model were shown in Figs. 3(c) and 3(d).

3.2.3 Slow-release mechanism

The XPS analysis of Ca/MgBC + NP after the 30-d leaching experiment in the three soils was performed to gain more insights into the slow-release behaviors of Ca/MgBC + NP (Fig. 4). Three forms of C related speciation were still identified, including C–C, C–O and O–C=O (Fig. 4(a)). The most significant different in the C 1s spectrum compared to Ca/MgBC + NP before experiment (Fig. S3) (Li et al., 2023a) was in the O–C=O peak, which was shifted and had a significantly reduced relative peak area in alkaline sandy and yellow soil, even for acidic red soil, after the addition of alkaline Ca/MgBC + NP, the relative peak area of O–C=O was reduced as slow-release occurred. The deconvolution results of O 1s were shown in Fig. 4(b), the two peaks belonging to O–H and M–O migrated after slow release in all three soils with consistent trends. Specifically, the relative peak area of O–H increased, and the peak area of M–O corresponding to MgO significantly decreased. In soil, on the one hand, MgO could exist in the form of Mg^{2+} , on the other hand, it could react with water to obtain $Mg(OH)_2$.

For the region of Mg 1s (Fig. 4(c)), the relative area of the peak of $Mg_3(PO_4)_2$ /struvite was significantly reduced, and even after experiment in red soil, no residual Mg-related stable substances were detected. This also indicated that the Mg-related substances in Ca/MgBC + NP could be well released in the soil. In the region of Ca 2p (Fig. 4(d)), except for the disappearance of $Ca(OH)_2$ in red soil, there were still three peaks, dominated by the two peaks of $CaCO_3$,

Table 2 Kinetic model parameters obtained from slow-release experiments

Model	Soil	Params	P	N
Zero-order	Yellow	k_0	0.01856	0.01789
		R^2	0.7711	0.6169
	Red	k_0	0.02283	0.02355
		R^2	0.8194	0.7137
	Sandy	k_0	0.02547	0.02688
		R^2	0.1264	0.6957
First-order	Yellow	k_1	-0.02425	-0.02399
		R^2	0.9064	0.8538
	Red	k_1	-0.03588	-0.03690
		R^2	0.9550	0.9412
	Sandy	k_1	-0.0383	-0.04118
		R^2	0.8640	0.8768
Higuchi	Yellow	k_2	0.08249	0.08451
		R^2	0.9747	0.9929
	Red	k_2	0.1132	0.1138
		R^2	0.9796	0.9867
	Sandy	k_2	0.1147	0.1174
		R^2	0.9865	0.9960
Hixson-Crowell	Yellow	k_3	0.007410	0.007260
		R^2	0.8714	0.7908
	Red	k_3	0.01030	0.01039
		R^2	0.9213	0.8969
	Sandy	k_3	0.01128	0.01200
		R^2	0.7298	0.8336
Baker-Lonsdale	Yellow	k_4	-0.01739	-0.01670
		R^2	0.7316	0.5513
	Red	k_4	-0.02088	-0.02161
		R^2	0.7866	0.6482
	Sandy	k_4	-0.02960	-0.02460
		R^2	0.5002	0.6494

both of which increased in area after the leaching experiment.

Further attention was given to the XPS spectra of both P and N nutrients. As shown in Fig. 4(e), most of the P-related substances in Ca/MgBC + NP were released during the slow-release experiments. Specifically, PO_4^{3-} was completely released from Ca/MgBC + NP, with only small amounts of HPO_4^{2-} and $H_2PO_4^-$ -related extremely stable substances present. In the XPS spectra of N 1s (Fig. 4(f)), the leaching experiment resulted in a better release of N-related substances. At the same time, an increase in the

percentage of relative peak area of NH_4^+ corresponding to struvite was observed in alkaline environments (sandy and yellow soils), and struvite is one of the most important substances for promoting plant growth.

3.3 Pot experiments

3.3.1 Effects of plants germination

To evaluate the effect of Ca/MgBC + NP on plant growth and its practical agricultural value, pot experiments were further designed. As shown in Figs. 5(a) and 5(b), both *Brassica chinensis* L. and

Spinacia oleracea L. seeds had the shortest germination time in the three soils with the addition of Ca/MgBC + NP(b), especially compared with Blank, which was more than two times shorter in Ca/MgBC + NP(b) treatment. Meanwhile, the Ca/MgBC + NP(b) treatment also had satisfactory germination rates, especially for *Brassica chinensis* L., which reached 100% in both red soil and sandy soil (Figs. 5(c) and 5(d)). This indicated that Ca/MgBC + NP(b) started to release N and P continuously once it reached the soil, which agreed very well with the slow-release performance. Overall, soil and fertilizer type had significant effects on the growth of both plants, with significant differences

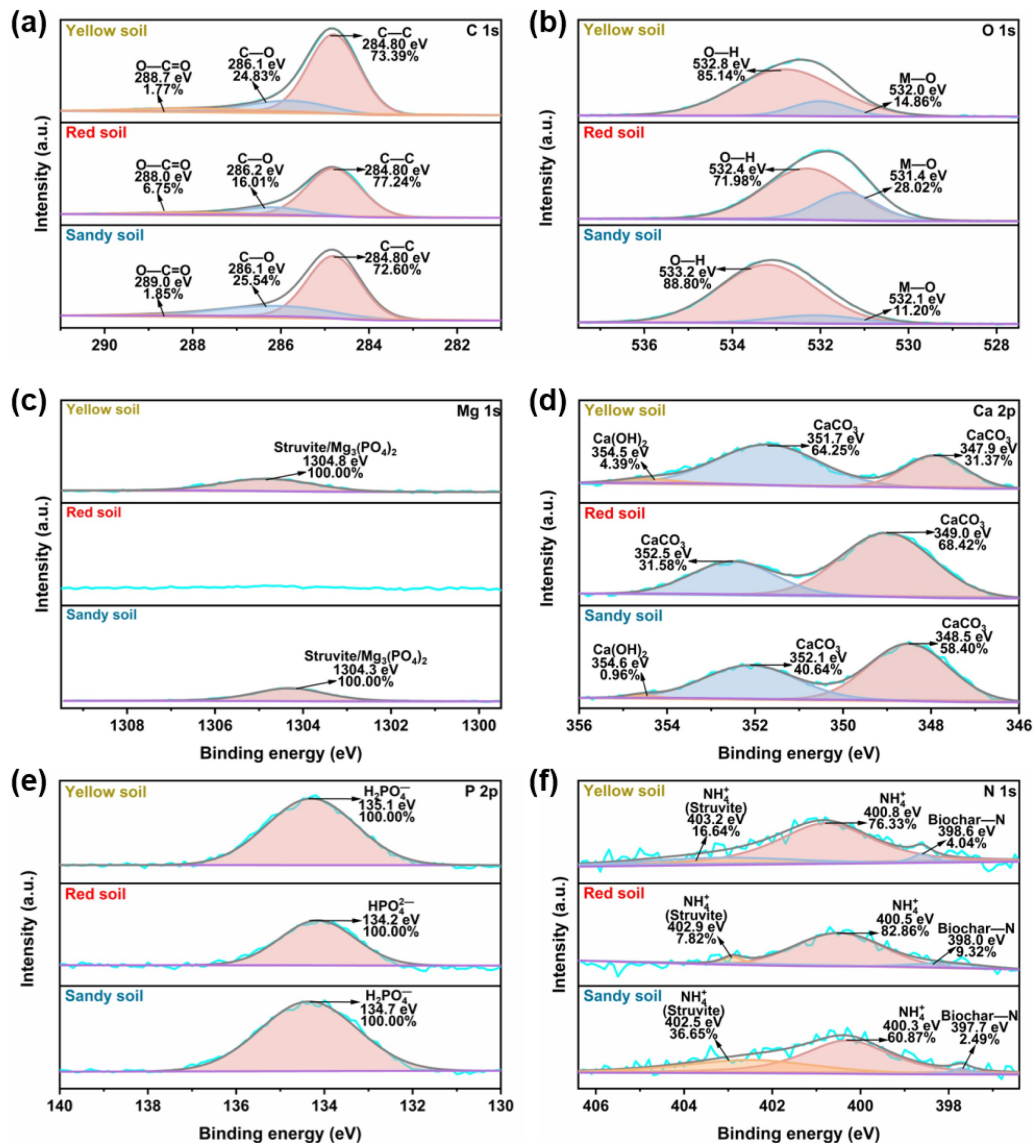


Fig. 4 XPS spectra of Ca/MgBC + NP after leaching experiment in the three soils: (a) C 1s, (b) O 1s, (c) Mg 1s, (d) Ca 2p, (e) P 2p, and (f) N 1s.

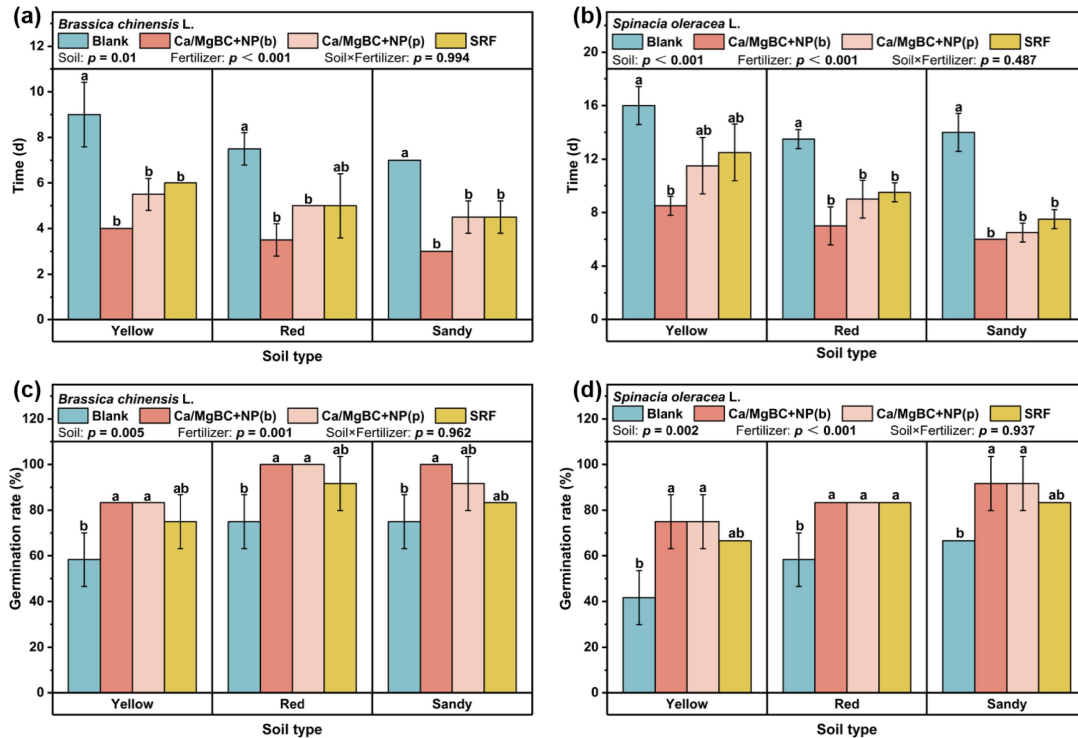


Fig. 5 (a, b) Days to germination and (c, d) germination ratio for *Brassica chinensis* L. seedlings and *Spinacia oleracea* L. seedlings fertilized with Blank, Ca/MgBC + NP(b), Ca/MgBC + NP(p) and SRF in three types of soil. Germination ratio were recorded 15 d after seeding. Lower case letters indicate significant differences among all treatments at $p < 0.05$, Lower case letters indicate significant differences among all treatments at $p < 0.05$, the 'p' in the legends of the figures indicates significant differences between soil treatment groups (between the three soil treatment groups), between fertilizer treatment groups (between the four fertilizer treatment groups), and between soil and fertilizer interactions.

between the Ca/MgBC + NP(b) and Blank treatments ($p < 0.05$). Previous studies have also demonstrated that P-loaded biochar materials could effectively improve grass seed germination (Yao et al., 2013).

3.3.2 Effects of plants growth

Since this study was conducted in winter (overall temperature < 10 °C), a pot experiment was conducted for a whole growth cycle of 90 d, with plant height above the soil recorded at 15-d intervals. It was found that the use of Ca/MgBC + NP(b) could also effectively increase the length and weight of shoot and root of both two plants. The application of Ca/MgBC + NP(b) resulted in a greater number of blades for *Brassica chinensis* L. and higher plant height on top of soil for *Spinacia oleracea* L. throughout the growth cycle (Figs. 6(a) and 6(b), Tables S4 & S5). This increasing trend was always significant between Ca/MgBC + NP(b) and blank. Comparing Ca/MgBC + NP(b) with SRF treatments, for *Brassica chinensis* L., there was a significant difference between the two in red and sandy

soil during the pre-developmental period (< 45 d for red soil, < 60 d for sandy soil) ($p < 0.05$), due to the *Brassica chinensis* L. tends to mature, we need to further analysis of shoot lengths and weights during the later stages of developmen. For *Spinacia oleracea* L., the two were consistently significantly different throughout the developmental period in red and sandy soil ($p < 0.05$).

After 90 d of growth, the two kinds of plant treated with Ca/MgBC + NP(b) showed an advantage in the growth of the three soils (Fig. 7). Compared with other treatments (Blank and SRF), the addition of Ca/MgBC + NP(b) had a better promotion of the average fresh weight, dry weight, shoot length and root length (Figs. 6(c) and 6(d), Table 3). In the case of *Brassica chinensis* L., there were significant differences between the Ca/MgBC + NP treatments and the blank and SRF treatments for all growth indices ($p < 0.05$), except for root length in the red soil. Whereas this significant difference was most pronounced in sandy soil, the average fresh weight, dry weight, shoot length, and root length of Ca/MgBC + NP(b) treatment was 1.25, 1.32,

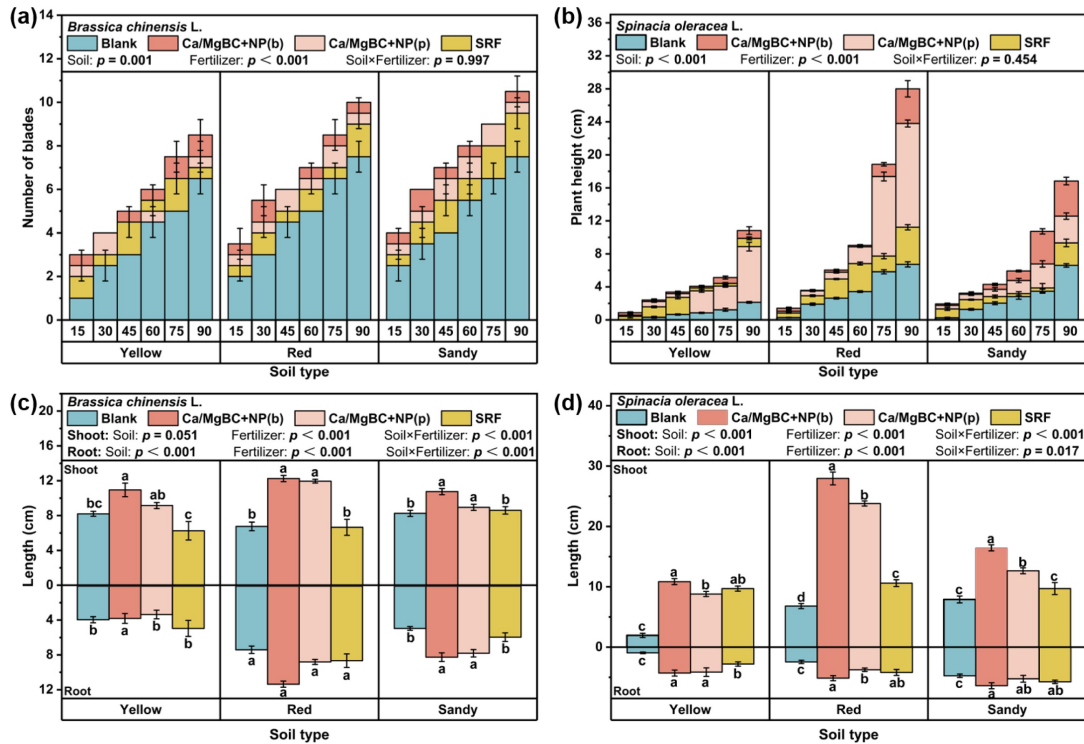


Fig. 6 (a) Number of blades of *Brassica chinensis* L. and (b) length of the upper part of the soil of *Spinacia oleracea* L. recorded in 15-d cycles; shoot and root length of (c) *Brassica chinensis* L. and (d) spinash fertilized with Blank, Ca/MgBC + NP(b), Ca/MgBC + NP(p) and SRF in three types of soil after 90 d of planting. Lower case letters indicate significant differences among all treatments at $p < 0.05$, Lower case letters indicate significant differences among all treatments at $p < 0.05$, the ‘p’ in the legends of the figures indicates significant differences between soil treatment groups (between the three soil treatment groups), between fertilizer treatment groups (between the four fertilizer treatment groups), and between soil and fertilizer interactions.

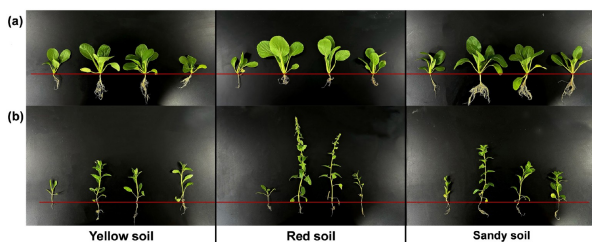


Fig. 7 Schematic images of (a) *Brassica chinensis* L. and (b) *Spinacia oleracea* L. plants after 90 d of planting in three types of soil. (Plants in each soil (in each small figure) were isolated from left to right from planting soils with no additions, Ca/MgBC + NP(b) applied, Ca/MgBC + NP (p) applied, and SRF applied).

1.72, and 1.81 times higher than those of SRF application. Similarly, this significant difference in sandy soil was also present in *Spinacia oleracea* L. pot experiments. The Ca/MgBC + NP treatment was 2.64, 2.84, 1.70, and 1.17 times more than the SRF treatment for the above four metrics. The fresh-dry ratio (fresh weight to dry weight ratio) and water content of two

plants did not change significantly, indicating that the content of water and organic matter were in approximate level among treatments (Shang et al., 2022).

In addition to the significant effect of the type of fertilizer added on plant growth ($p < 0.05$), the different types of soil also had a significant effect ($p < 0.05$). This is because red and yellow soils are more favorable for stem and leaf growth as they are clay, and the greater stickiness of the soil (red soil), the less favorable it is for root development, while sandy soils are more favorable for root growth. However, despite the poorer fertilizer retention capacity of sandy soil, the application of Ca/MgBC + NP(b) was still able to promote root growth obviously. All the results proved that Ca/MgBC + NP could effectively promote the growth of *Brassica chinensis* L. and *Spinacia oleracea* L., and the promotion was more evident in the sandy soil (shoot and root growth were different compared to Blank and SRF treatments ($p < 0.05$)). In addition to the effect of the inherent nature of clay on root

Table 3 Growth indicators of *Brassica chinensis* L. and *Spinacia oleracea* L. after application of different fertilizer treatments (the 90th day)

Crop	Soil	Sample	Fresh weight (g)		Dry weight (g)	
			Shoot	Root	Shoot	Root
<i>Brassica chinensis</i> L.	Yellow	Blank	0.9783±0.0971d	0.0948±0.0070b	0.0990±0.0144c	0.0134±0.0040c
		Ca/MgBC+NP(b)	4.6027±0.1563a	0.5884±0.0913a	0.4864±0.0328a	0.0698±0.0095a
		Ca/MgBC+NP(p)	3.5420±0.1546b	0.5363±0.0390a	0.3488±0.0231b	0.0663±0.0069a
		SRF	2.0771±0.2631c	0.3170±0.0646c	0.2184±0.0776c	0.0393±0.0085b
	Red	Blank	0.7901±0.0157d	0.0716±0.0029b	0.0854±0.0111 d	0.0123±0.0087b
		Ca/MgBC+NP(b)	4.1379±0.2471a	0.2322±0.0803a	0.3838±0.0068a	0.0253±0.0069a
		Ca/MgBC+NP(p)	3.5176±0.2468b	0.1685±0.0129ab	0.3364±0.0251b	0.0215±0.0098ab
		SRF	2.0241±0.0693c	0.1486±0.0033ab	0.2037±0.0168c	0.0180±0.0017ab
	Sandy	Blank	1.4717±0.0267d	0.0922±0.0099d	0.1360±0.0090d	0.0147±0.0110c
		Ca/MgBC+NP(b)	4.7707±0.1796a	1.1557±0.0426a	0.4811±0.0397a	0.1375±0.0122a
		Ca/MgBC+NP(p)	3.6962±0.1142b	0.6483±0.0062b	0.3791±0.0278b	0.0826±0.0038b
		SRF	2.8719±0.1742c	0.5655±0.0161c	0.2715±0.0437c	0.0694±0.0112b
<i>Spinacia oleracea</i> L.	Yellow	Blank	0.1292±0.0112d	0.0046±0.0009b	0.0199±0.0014c	0.0020±0.0006b
		Ca/MgBC+NP(b)	1.0584±0.0276a	0.0415±0.0076a	0.1126±0.0123a	0.0101±0.0028a
		Ca/MgBC+NP(p)	0.5310±0.0888b	0.0296±0.0129a	0.0679±0.0117b	0.0074±0.0015a
		SRF	0.3818±0.0270c	0.0258±0.0016ab	0.0463±0.0062b	0.0062±0.0013ab
	Red	Blank	0.2593±0.0058d	0.0080±0.0013c	0.0309±0.0015c	0.0034±0.0011c
		Ca/MgBC+NP(b)	3.5624±0.0248a	0.0438±0.0069a	0.3224±0.0477a	0.0094±0.0011a
		Ca/MgBC+NP(p)	1.7531±0.0759b	0.0263±0.0064b	0.1836±0.0422b	0.0071±0.0012ab
		SRF	0.5475±0.0308c	0.0208±0.0048bc	0.0647±0.0072c	0.0051±0.0012bc
	Sandy	Blank	0.2875±0.0064d	0.0106±0.0019c	0.0316±0.0038c	0.0038±0.0016a
		Ca/MgBC+NP(b)	1.4903±0.1167a	0.4562±0.0115a	0.1478±0.0310a	0.1110±0.0057a
		Ca/MgBC+NP(p)	1.0049±0.1247b	0.0332±0.0084b	0.1157±0.0297ab	0.0078±0.0013b
		SRF	0.7067±0.0502c	0.0314±0.0035bc	0.0824±0.0086bc	0.0086±0.0016b

Notes: Different letters in the same column represent significantly different ($p < 0.05$).

development, the better development of shoot in red soil (especially *Spinacia oleracea* L.) was attributed to a greater release of N and the more favorable release of nutrients from our material under acidic conditions (in good agreement with the results of slow-release experiments in water and soil).

To further confirm the mechanism of crop growth promotion by application of Ca/MgBC + NP, XRD pattern of Ca/MgBC + NP in sandy soil after planting *Brassica chinensis* L. and *Spinacia oleracea* L. was tested (Fig. S4). Compared to the Ca/MgBC + NP before planting (Fig. S5) (Li et al., 2023a), the characteristic peaks of struvite and $Mg_3(PO_4)_2$ all disappeared, proving the contributing role of the two during planting. $CaCO_3$ was able to stabilize in the soil and therefore its characteristic peaks remained (29.39° , 39.42° , 43.17° , 47.47° and 48.53°). In addition, peaks of SiO_2 (20.86° , 26.64° , 36.55° , 40.29° , 42.45° , 45.80° ,

50.14° , 59.96° , 67.74° , 68.14° , 73.47° , 75.66° , and 77.67°), which is abundant in the soil, appeared on the pattern, as well as peaks of andesine (21.87° and 27.85°).

In summary, the promoting effect of Ca/MgBC + NP on plant growth is primarily attributed to its ability to continuously release N and P. The excellent slow-release performance of Ca/MgBC + NP(b) better matches the nutrient assimilation rate of plants, which is especially favorable for long-term stable nutrient accumulation by plants (Luo et al., 2021). On the other hand, the presence of struvite crystals and Mg-related substances in Ca/MgBC + NP also provide nutrients required for plant growth (combined with the slow-release mechanism and XRD, XPS spectra of Ca/MgBC + NP). The promotion of Ca/MgBC + NP(p) was not as good as that of Ca/MgBC + NP(b) due to the large particle size of the beads, which could increase the pore

space between soil particles and facilitated the respiration of root system, while the powdered fertilizer was more susceptible to volatilization and loss.

Finally, the total cost of Ca/MgBC + NP (including the cost of raw materials for production and the cost of energy consumption) is lower compared to the expenditure on purchasing SRFs (Tables S6 and S7), indicating that the economic viability of Ca/MgBC + NP is more promising. For the benefit analysis of Ca/MgBC + NP, it mainly includes environmental benefit, economic benefit and scalability analysis. Among them, the low cost, environmental benefits and environmental protection characteristics of Ca/MgBC + NP make Ca/MgBC + NP have better market potential and may bring higher economic benefits and better scalability. The environmental benefits of Ca/MgBC + NP are mainly based on three aspects: reducing ammonia volatilization, promoting phosphorus cycling and soil improvement. Through the comparative analysis of Ca/MgBC + NP and SRF, Ca/MgBC + NP improved the above indexes of soils better than SRF, therefore, it can be seen that the environmental benefits of Ca/MgBC + NP are also very considerable.

3.4 Effects on soil physicochemical properties

Previous studies have found that biochar helps to improve the physicochemical properties of soil (Hossain et al., 2020). Most of the current research focuses on the effects of various types of modified biochar directly on the physicochemical properties of soils, with fewer studies on soils where crops are grown. Based on this, this study investigated the pH, cation exchange, and organic carbon of the three soils after 90 d of planting *Brassica chinensis* L. to examine the effect of Ca/MgBC + NP on the physicochemical properties of the planted soil and further examined the ability of Ca/MgBC + NP to remediate the soil for heavy metals.

3.4.1 Soil pH regulation

Soil pH affects the effectiveness of soil nutrients. As shown in Fig. 8, the pH value of the soil planted with *Brassica chinensis* L. showed different degrees of increase after Ca/MgBC + NP application, rising by 1.0 unit (yellow soil), 1.4 units (red soil), and 0.8 units (sandy soil). *Brassica chinensis* L., as an alkaline-loving plant, releases CO_3^{2-} during planting, so the pH of the post-planting soil also increased in the Blank treatment (0.3 units (yellow soil), 0.4 units (red soil) and 0.2 units (sandy soil)). While SRF as a weakly acidic slow-release fertilizer, resulted in a decrease in soil pH after planting. The application of Ca/MgBC +

NP to increase the pH value of the soil was based on two main aspects. On the one hand, most of the BC showed alkalinity (pH = 9–12), While SRF, as a weakly acidic slow-release fertilizer, led to a decrease in soil pH after planting.

The application of Ca/MgBC + NP to increase soil pH is based on two main aspects. On the one hand, most BC are alkaline (pH = 9–12), and the alkaline substances would release after entering the soil (Zhang et al., 2025a). On the other hand, ligand exchange reactions between functional groups on the surface of Ca/MgBC + NP after entering the soil deplete protons from the soil environment (Guo et al., 2010; Herath et al., 2015).

3.4.2 Soil fertilizer retention

Soil nutrients are one of the most important indicators of soil fertility, which directly affects crop growth and yield. In Section 3.3, it is clear that Ca/MgBC + NP could promote plant growth more effectively than SRF. Further research found that soil nutrients were effectively improved after using Ca/MgBC + NP and SRF. After 90 d of cabbage planting, the AP content in the soil with Ca/MgBC + NP application was 2.00 and 1.67 times (yellow and red soil), 4.20 and 3.50 times (sandy soil) higher than those of Blank and SRF treatments (Fig. 8), respectively. The significant differences in the development of our *Brassica chinensis* L. shoot and root were also most obvious in the sandy soil. For $\text{NH}_4^+\text{-N}$, Ca/MgBC + NP treatments were 2.37 and 1.06 times (yellow soil), 1.64 and 1.23 times (red soil), 2.11 and 1.76 times (sandy soil) more than Blank and SRF treatments, respectively.

It can be seen that the application of Ca/MgBC + NP was able to increase the nutrient content of the soil while promoting plant growth. This is due to that Ca/MgBC + NP, as a biochar-based material, contains a high level of fast-acting nutrients, which could be directly imported into the soil (which coincides with the slow-release behavior of Ca/MgBC + NP). Moreover, Ca/MgBC + NP is a kind of porous material, its pore structure not only reduces the leaching of nutrients, and leads to the fixation of nutrients for slow-release, but also provides a suitable habitat for soil microorganisms, thus improving soil fertilizer retention (Ding et al., 2016).

3.4.3 Soil carbon sequestration and increased organic matter

Soil organic matter (SOM) is one of the main sources of plant nutrients, which promotes plant growth and development, improves soil physical properties,

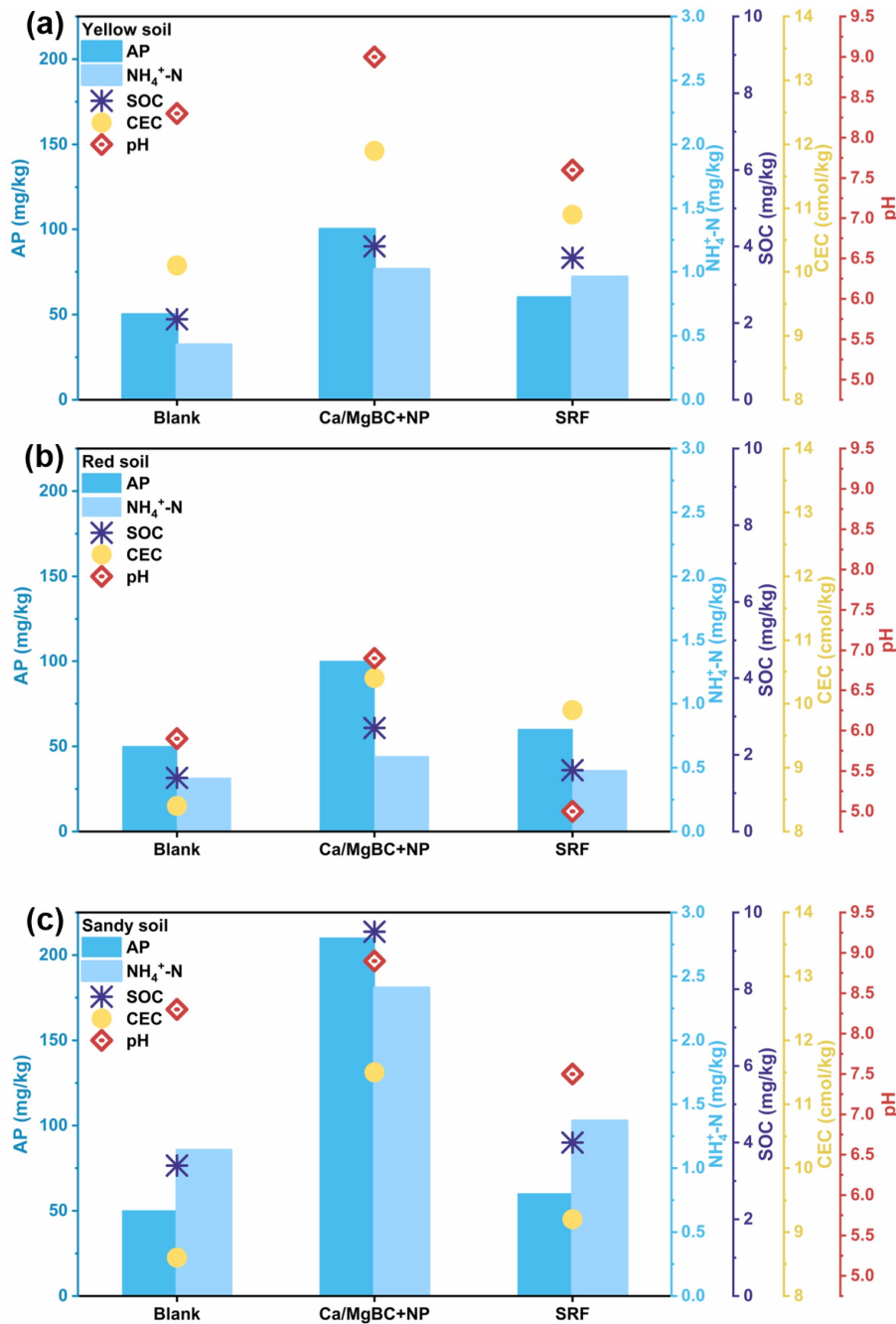


Fig. 8 Effect of Blank, Ca/MgBC + NP and SRF treatments on AP, NH₄⁺-N, SOC, CEC and pH in (a) yellow soil, (b) red soil and (c) sandy soil after planting *Brassica chinensis* L. for 90 d.

promotes soil biological activity and improves soil fertility and buffering. The content and changes in SOM are usually assessed by measuring the SOC content. Application of Ca/MgBC + NP was more effective in increasing SOC content compared to unplanted soil. As shown in Fig. 8, SOC increased by 90.48% and 53.85% (yellow soil), 92.86% and 68.75%

(red soil), and 179.41% and 137.50% (sandy soil) with Ca/MgBC + NP application compared to Blank and SRF treatments. The increase in organic carbon was mainly due to Ca/MgBC + NP contained carrier biochar, which itself contained high organic carbon, leading to an effective increase in the carbon stock of the soil.

The effective increase of SOC means the increase of organic matter. The increase in organic matter is based on two aspects. On the one hand, it has been found that the application of biochar improves the activity of soil microorganisms, accelerates the decomposition of humus, resulting in an increase in the organic matter content of the soil (Hua et al., 2012). On the other hand, the aromatic functional groups on the surface of biochar passivate in the soil to form a protective matrix, which improves the stability of organic matter and makes it less susceptible to decomposition, thus leading to an increase in organic matter content indirectly (Guo et al., 2017).

3.4.4 Increased soil cation exchange capacity

The value of CEC assesses the soil's ability to absorb, retain and exchange cations, is one of the most important indicators of soil fertility retention. Increasing the soil CEC value stabilize organic matter, thus promoting adequate nutrient uptake by plants. In our study, after 90 d of planting *Brassica chinensis* L., all the three treatments exhibited increase in CEC in all soils compared to unplanted soils. And the CEC values increased more in the soils after Ca/MgBC + NP application compared to the Blank and SRF treatments (17.82% and 9.17% for yellow soil, 23.81% and 5.05% for red soil, 33.72% and 6.98% for sandy soil) (Fig. 8). On the one hand, our Ca/MgBC + NP was shown to have an electronegative surface by zeta potential tests in our previous studies, which led to its ability to enhance the adsorption of salt ions by soil colloids upon entering the soil (Zhang et al., 2025b). On the other hand, the carboxyl functional group on its surface is able to adsorb cations, thus enhancing the CEC value (Gao et al., 2019).

3.4.5 Contaminated soil remediation

Most of the current studies are devoted to the direct

remediation of contaminated agricultural land using biochar, while the remediation potential of biochar-based fertilizers lacks exploration. As shown in Fig. 9, our Ca/MgBC + NP immobilized all seven heavy metals in the three soils, the immobilization rate was higher than that of the immobilization experiments in water (Fig. S6) (Li et al., 2023a), which is due to the soil also could immobilize heavy metals by itself. In comparison with Blank, the addition of Ca/MgBC + NP significantly enhanced the immobilization of heavy metals. In all three soils, the heavy metal immobilization ratios of Blank treatment were almost at less than 40%, which increased by more than 100% with the addition of Ca/MgBC + NP, with the most significant increase in the immobilization of Hg and Zn in sandy soil (4.5 and 4.6 times that of Blank).

Among the three soils, heavy metal content decreased in the following order: yellow soil > red soil > sandy soil. The texture of the soil plays an important role in its ability to immobilize heavy metals. There was a significant difference in the content of clay particles in soils of different textures (clay > sandy soil), with clay soils having a higher content of clay particles, and the large specific surface of clay particles being the main carrier of heavy metal enrichment, which makes it easier to adsorb heavy metals. Also, the acidity and alkalinity of the soil has an effect on the soil immobilization of heavy metals, which tend to form stable hydroxides or precipitates under alkaline conditions. Therefore, it can be seen that in the study, the immobilization capacity was best in yellow soil and worst in sandy soil in the blank treatment. With the addition of Ca/MgBC + NP, the stronger alkalinity of biochar in red soil increased the soil pH and accelerated the transformation of heavy metal ions to a more stable state (Zhang et al., 2025a).

The enhanced immobilization is also related to the physicochemical properties of Ca/MgBC + NP. On the one hand, the FTIR and XPS spectra of Ca/MgBC + NP

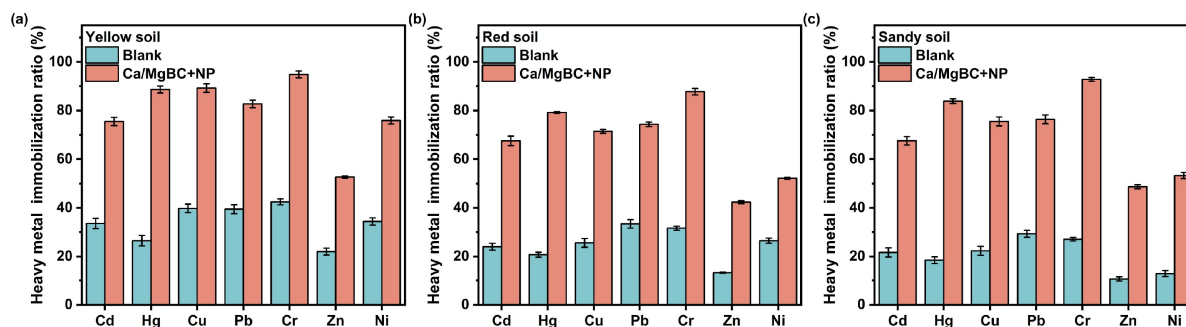


Fig. 9 Effect of Ca/MgBC + NP addition on Cd, Hg, Cu, Pb, Cr, Zn, Ni immobilization in (a) yellow soil, (b) red soil, and (c) sandy soil. Reaction time: 24 h.

(Fig. S5) revealed that the surface of Ca/MgBC + NP was rich in oxygen-containing functional groups (carboxyl, hydroxyl, and phenolic hydroxyl), which were able to form stable complexes with heavy metal ions, thus realizing the adsorption and immobilization of heavy metals. The high specific surface area and porous structure of Ca/MgBC + NP also provide more adsorption sites for it. On the other hand, the addition of Ca/MgBC + NP could also increase the pH value of the soil, thus promoting the conversion of heavy metal ions to more stable precipitates (Palansooriya et al., 2022; Lyu et al., 2024). For Cd, Cu, Pb, Zn, and Ni, these heavy metal ions were immobilized mainly through adsorption by forming complexes with oxygenated functional groups on the surface of Ca/MgBC + NP (Du et al., 2024; Kang et al., 2024; Ma et al., 2024; Yang et al., 2024). Cr mainly exists as Cr(III) and Cr(VI) in the soil, and the oxygen-containing functional groups on the surface of Ca/MgBC + NP are able to form stable complexes with Cr(III), which reduces its mobility in the soil. In addition, the alkaline environment of Ca/MgBC + NP helps to reduce Cr(VI) to Cr(III), which further reduces its toxicity and mobility (Chen et al., 2022; Li et al., 2023b). Hg exists in soil mainly in the form of Hg(II), which has high mobility and toxicity. The oxygen-containing functional groups on the surface of Ca/MgBC + NP are able to form stable complexes with Hg(II), which reduces its mobility in the soil. In addition, the porous structure and high specific surface area of biochar provide more sites for Hg(II) adsorption (Yang et al., 2021).

3.5 Principal component analysis

The PCA output extracted 2 factors that were able to explain 91.67% of the 8 indicators. The ranking of the constructed composite scores of the obtained principal component scores was consistent with the effect of our plant growth and soil property improvement (Table S8), with sandy soil > red soil > yellow soil. Through the factor loadings (Fig. S7), Factor 1 explained 52.67% of the variance and is mainly related to the soil property-related indicators, as well as a negative correlation with the water retention capacity. Factor 2 explained 39.00% of the variance and provides a good positive correlation with soil slow-release behavior, while being negatively correlated with soil CEC and pH. This partly explained the inherent poor water and fertilizer retention capacity of sandy soils but the best promotion effect.

4 Conclusions

In this study, we systematically evaluated the potential

of Mg-modified biochar beads (Ca/MgBC + NP) loaded with struvite as the slow-release fertilizers and soil amendment in agricultural practices. A series of studies, including fertilizer property determination, potting experiments, soil property testing and heavy metal immobilization, demonstrated the remarkable effects of Ca/MgBC + NP in promoting crop growth, improving soil properties and remediating soil heavy metal pollution.

1) Reducing environmental pollution and promoting the development of sustainable agriculture. Ca/MgBC + NP, as a kind of slow-release fertilizer, could significantly improve the utilization efficiency of N and P and reduce the loss of nutrients, which not only improves the economic benefits of fertilizer, but also reduces the environmental pollution caused by the excessive use of chemical fertilizer. Through kinetic analysis, we found that the slow-release mechanism of Ca/MgBC + NP was mainly a diffusion mechanism, which provided theoretical support for optimizing fertilizer formulation and application. Furthermore, Ca/MgBC + NP showed significant crop growth promotion effects in different soil types, including yellow soils, sandy soils and red soils. Especially in sandy soil, its growth-promoting effect on *Brassica chinensis* L. and *Spinacia oleracea* L. was the most significant. This validation of multiple soil types and multiple crops provides a scientific basis for the wide application of Ca/MgBC + NP.

2) Improved soil properties and realized soil remediation. In acidic red soils, Ca/MgBC + NP can effectively regulate soil pH from 5.5 to 6.9, and in sandy soils, it could significantly increase the CEC and SOC of the soil by 38.55% and 265.38%. This comprehensive amelioration effect provides a new solution to solve the problems of soil acidification and sandy soil. Meanwhile, Ca/MgBC + NP performed well in the remediation of soil heavy metal pollution, with good immobilization effects on many heavy metals (such as Cd, Hg, Cu, Pb, Cr, Zn and Ni). Especially, the immobilization rate of Cr and Hg is more than 80%, and the immobilization rate of Cr in all soils even reaches 90%.

3) Considerable application prospects. Through long-term potting experiments, Ca/MgBC + NP showed good slow-release performance and soil improvement effect in different types of soils throughout the growth cycle. This long-term application effect provides an important theoretical support for the wide application of Ca/MgBC + NP in agricultural practice, and the multifunctionality of Ca/MgBC + NP, which has comprehensive advantages in slow-release fertilizers, soil improvement, and heavy-metal pollution

remediation, makes its application in agricultural practice promising.

Evidently, Ca/MgBC + NP, as a green, environmentally friendly, and low-cost soil slow-release fertilizer, has multiple functions of promoting crop growth, improving soil properties, and remediating soil heavy metal contamination. More importantly, the ability of Ca/MgBC + NP to promote crop growth with different nutrient and pH requirements in soils of varying properties, fully demonstrating the feasibility and universality of Ca/MgBC + NP in agricultural practices.

CRediT Authorship Contribution Statement

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Hanbing Li, Li Wang and Yiwen Wang. The first draft of the manuscript was written by Hanbing Li and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conflict of Interests 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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