

Supplementary material

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

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Text. S1 Indoor simulated soil column leaching experiment design scheme

The soil column was made of a chromatography column with an inner diameter of 3 cm and a height of 30 cm, and the bottom end of the column was sealed by a switching conduit control. The bottom of the chromatographic column was flatly laid with quartz sand particles (acid washed with 2.0 mol/L concentrated sulfuric acid, and washed with DI after 24 h). After laying a layer of 200 mesh nylon mesh, loaded with mixture of soil, fertilizer sample and quartz sand, compacted and covered with quartz sand to prevent the addition of water resulting in the soil mixture being disturbed. The loaded chromatography column was fixed in a test tube holder, and a beaker was placed at the bottom for collecting the leachate solution.

Text. S2 Slow-release experimental water addition frequency scheme

The precipitation in Xi'an in the last ten years was shown in Table S1 (Source: Xi'an Municipal Bureau of Statistics, Xi'an Statistical Yearbook). As shown in Table S1, in the past ten years, the average daily precipitation in Xi'an was 1.9 mm, and the total precipitation days was 101 d (27.7% of the year), so the pre-setting of the leaching experiment was to add water every nine days to simulate precipitation, and the height of precipitation each time was 17.1 mm, according to the diameter of the used Plexiglas tube, the calculated amount of water added was 12.1 mL. Considering the loss of water in the soil, the actual soil column leaching experiments were carried out by adding water every other day, 50 mL each time.

Text. S3 Principal component analysis method

Eight data related to water retention and slow-release properties as well as soil physicochemical properties in the three soils were standardized (Z-score method) by SPSS 27, including water retention capacity of the soils after 29 days, cumulative release of P and N slow release for 30 d, and TP, $\text{NH}_4^+\text{-N}$, pH, SOC, and CEC of the soils after planting. Suitability of factor analysis was tested by the KOM test and the Bartlett's sphere, and there was correlation between the indicators if the KOM value was > 0.5 and the Sig value was < 0.05 . The two results of this study satisfied

the above requirements, which proved that the research data were suitable for factor analysis method.

The principal components in PCA are linear combinations of indicator variables, the coefficient of the linear combination of indicator variable data enables to obtain the data related to the principal component scores (Eq. S1).

$$F_n = u_{n1}ZX_1 + u_{n2}ZX_2 + \dots + u_{nn}ZX_n, \quad (S1)$$

where ZX is the standardized value of the indicator variable, u is the linear combination coefficient (obtained by loading coefficients), F is the principal component and n is the number of factors.



Fig. S1 Synthesis scheme of Ca/MgBC + NP.

The corn stalk used in this study was sourced from Shanxi Province, China. Dried at 60°C for 24 h, then ground and passed through a 60-mesh sieve. Sodium alginate (SA, Chemical pure, China), magnesium chloride hexahydrate (MgCl₂·6H₂O, Analytical reagent, China), calcium chloride dihydrate (CaCl₂·2H₂O, Analytical reagent, China), potassium dihydrogen phosphate (KH₂PO₄, Analytical reagent, China), ammonium chloride (NH₄Cl, Guaranteed reagent, China), sodium hydroxide (NaOH, Analytical reagent, China) and all other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (DI, PLUS-E2R20UV, EPED, China) was used for all experiments.

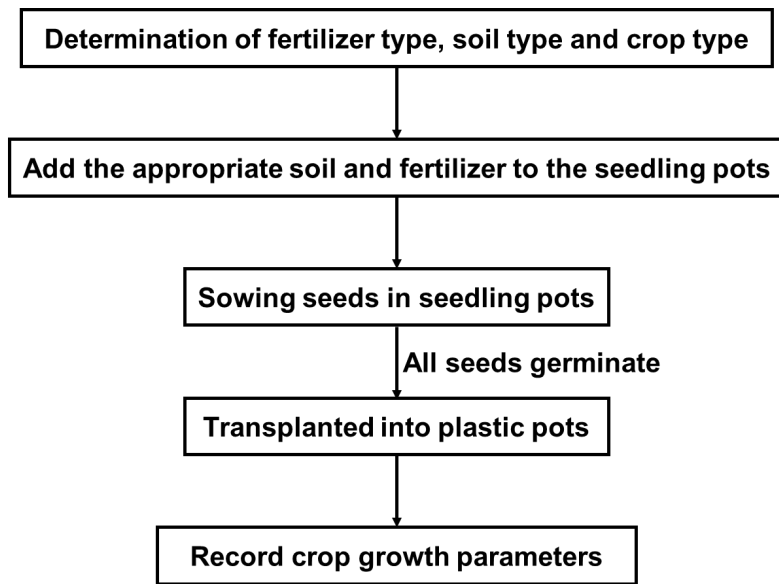


Fig. S2 Schematic of the workflow of the potting experiment.

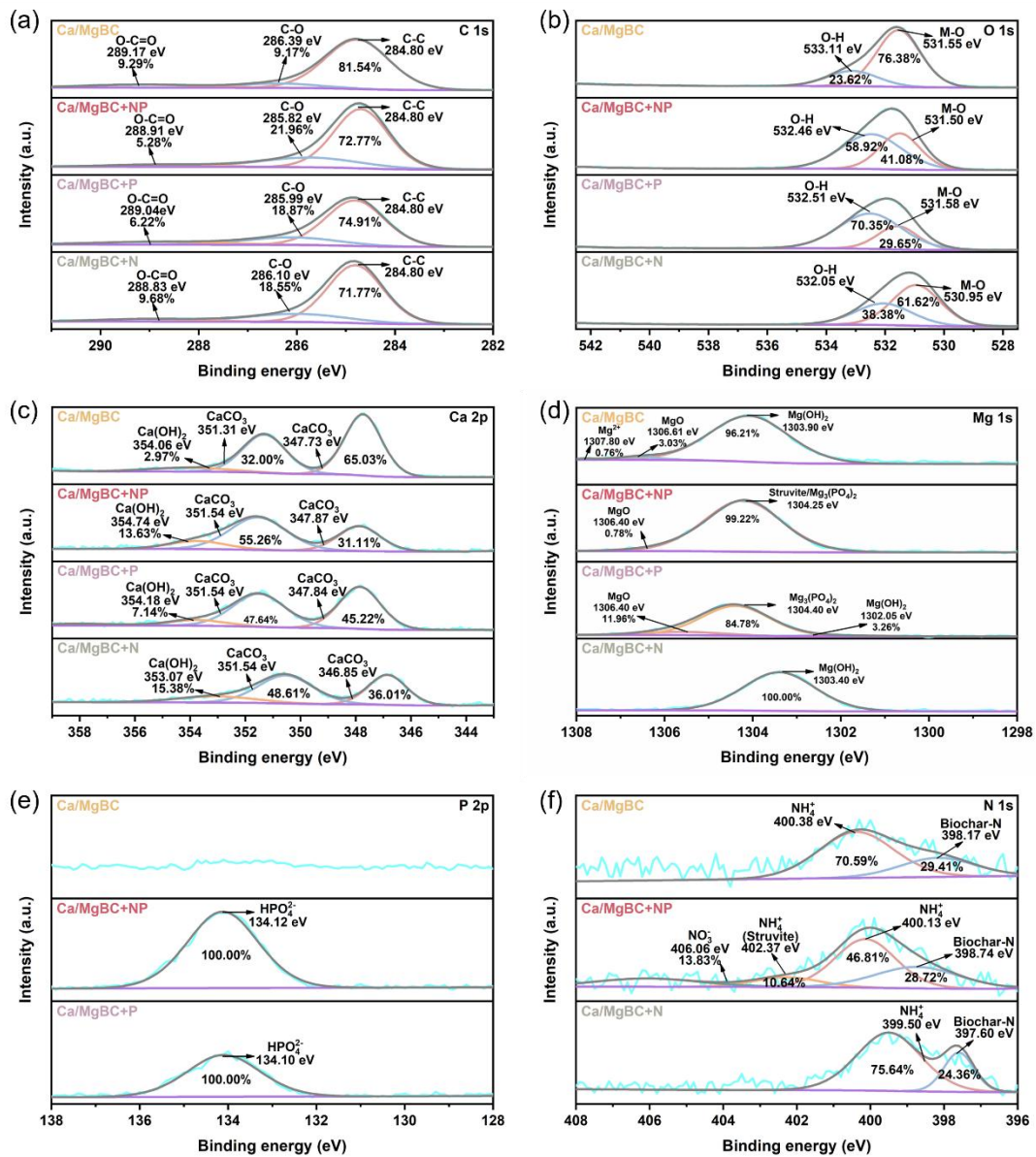


Fig. S3 XPS spectra of Ca/MgBC (before adsorption) and Ca/MgBC + NP (after adsorption): (a) C 1s, (b) O 1s, (c) Ca 2p, (d) Mg 1s, (e) P 2p and (f) N 1s. Reprinted from (Li et al., 2023) with permission from Elsevier.

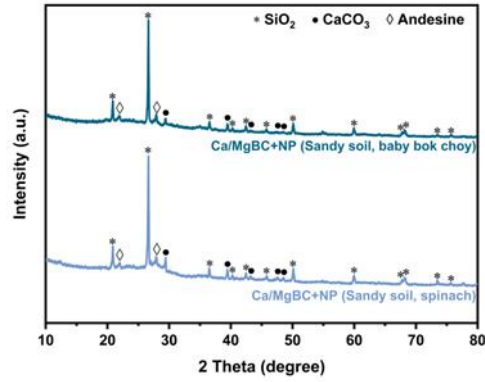


Fig. S4 XRD patterns of Ca/MgBC + NP in sandy soil after planting *Brassica chinensis* L. and *Spinacia oleracea* L.

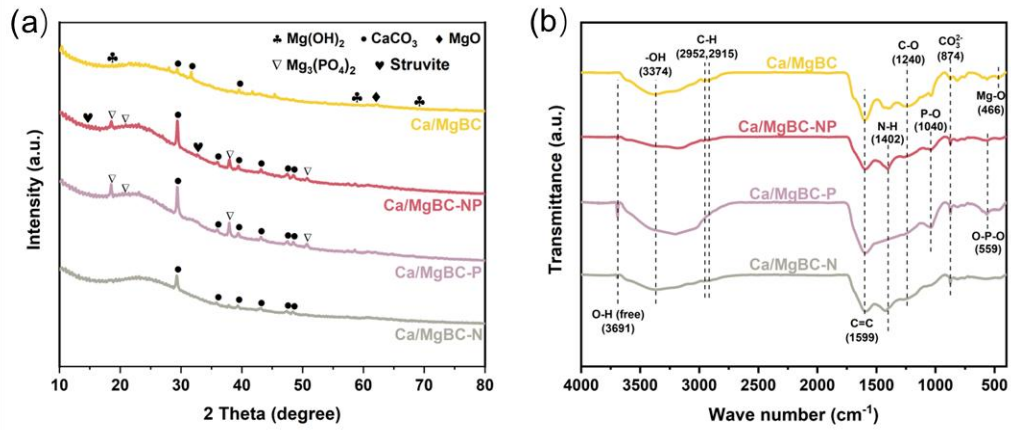


Fig. S5 (a) XRD patterns and (b) FTIR patterns of Ca/MgBC (before adsorption) and Ca/MgBC + NP (after adsorption). Reprinted from (Li et al., 2023) with permission from Elsevier.

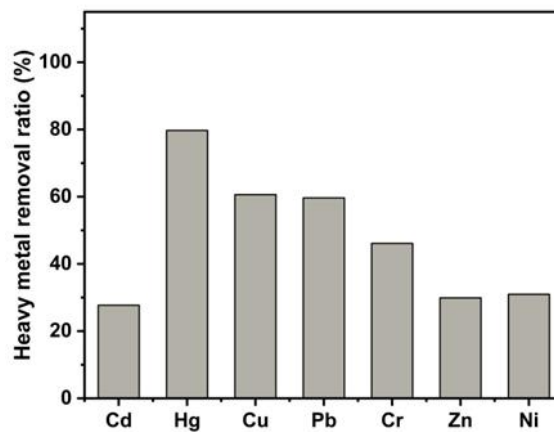


Fig. S6 Removal ratio of Cd, Hg, Cu, Pb, Cr, Zn and Ni from water by Ca/MgBC + NP. Adsorbent dosage: 1.0 ± 0.01 g/L, temperature $25^\circ\text{C} \pm 1^\circ\text{C}$, initial concentrations 50 mg/L, 150 r/min, pH 4.0 ± 0.5 , reaction time 24 h.

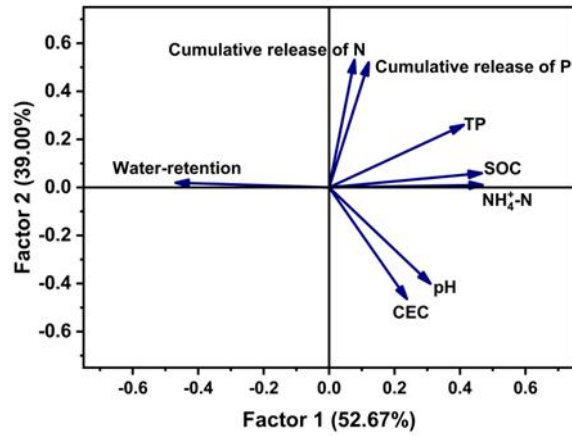


Fig. S7 Factor loadings of Factor 1 and Factor 2 (91.67%).

Table S1 The precipitation in Xi'an in the last ten years.

Item	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	Average
Daily precipitation (mm)	1.3	1.9	1.8	1.6	2.0	1.6	1.9	1.9	2.9	1.6	1.9
Days of rain and snow (d)	75	99	104	98	120	103	97	108	116	88	101

Table S2 Experimental treatment design, soil type and type of fertilizer applied.

Treatments	Type of fertilizer applied	Soil type	Crop type
1	Blank	Yellow soil	<i>Brassica chinensis</i> L.
2			<i>Spinacia oleracea</i> L.
3		Red soil	<i>Brassica chinensis</i> L.
4			<i>Spinacia oleracea</i> L.
5		Sandy soil	<i>Brassica chinensis</i> L.
6			<i>Spinacia oleracea</i> L.
7	Ca/MgBC+NP(b)	Yellow soil	<i>Brassica chinensis</i> L.
8			<i>Spinacia oleracea</i> L.
9		Red soil	<i>Brassica chinensis</i> L.
10			<i>Spinacia oleracea</i> L.
11		Sandy soil	<i>Brassica chinensis</i> L.
12			<i>Spinacia oleracea</i> L.
13	Ca/MgBC+NP(p)	Yellow soil	<i>Brassica chinensis</i> L.
14			<i>Spinacia oleracea</i> L.
15		Red soil	<i>Brassica chinensis</i> L.
16			<i>Spinacia oleracea</i> L.
17		Sandy soil	<i>Brassica chinensis</i> L.
18			<i>Spinacia oleracea</i> L.
19	SRF	Yellow soil	<i>Brassica chinensis</i> L.
20			<i>Spinacia oleracea</i> L.
21		Red soil	<i>Brassica chinensis</i> L.
22			<i>Spinacia oleracea</i> L.
23		Sandy soil	<i>Brassica chinensis</i> L.
24			<i>Spinacia oleracea</i> L.

Table S3 Additions to different fertilizer samples.

Fertilizer sample	Additions to fertilizer samples (g/600g soil)	
	<i>Brassica chinensis</i> L.	<i>Spinacia oleracea</i> L.
Blank	0.000	0.000
Ca/MgBC+NP(b)	1.797	2.644
Ca/MgBC+NP(p)	1.797	2.644
SRF	0.986	1.450

Table S4 Number of blades of *Brassica chinensis* L. after application of different fertilizer treatments (every 15 days as a recording cycle).

Day	Soil	Fertilizer sample			
		Blank	Ca/MgBC+NP(b)	Ca/MgBC+NP(p)	SRF
15	Yellow	1.0±0.0b	3.0±0.0a	2.5±0.7a	2.0±0.0ab
	Red	2.0±0.0b	3.5±0.7a	3.0±0.0ab	2.5±0.7ab
	Sandy	2.5±0.7b	4.0±0.0a	3.5±0.7ab	3.0±0.0ab
30	Yellow	2.5±0.7b	4.0±0.0a	4.0±0.0a	3.0±0.0ab
	Red	3.0±0.0c	5.5±0.7a	4.5±0.7ab	4.0±0.0bc
	Sandy	3.5±0.7c	6.0±0.0a	5.0±0.0ab	4.5±0.7bc
45	Yellow	3.0±0.0b	5.0±0.0a	4.5±0.7a	4.5±0.7a
	Red	4.5±0.7b	6.0±0.0a	6.0±0.0a	5.0±0.0ab
	Sandy	4.0±0.0c	7.0±0.0a	6.5±0.7ab	5.5±0.7b
60	Yellow	4.5±0.7b	6.0±0.0a	5.0±0.0ab	5.5±0.7ab
	Red	5.0±0.0b	7.0±0.0a	6.5±0.7a	6.0±0.0ab
	Sandy	5.5±0.7b	8.0±0.0a	7.5±0.7a	6.5±0.7ab
75	Yellow	5.0±0.0b	7.5±0.7a	6.5±0.7ab	6.5±0.7ab
	Red	6.5±0.7c	8.5±0.7a	8.0±0.0ab	7.0±0.0bc
	Sandy	6.5±0.7b	9.0±0.0a	9.0±0.0a	8.0±0.0a
90	Yellow	6.5±0.7b	8.5±0.7a	7.5±0.7ab	7.0±0.0ab
	Red	7.5±0.7b	10.0±0.0a	9.5±0.7a	9.0±0.0a
	Sandy	7.5±0.7b	10.5±0.7a	10.0±0.0a	9.5±0.7a

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

Table S5 Length of the upper part of the soil of *Spinacia oleracea* L. after application of different fertilizer

treatments (every 15 days as a recording cycle).

Day	Soil	Fertilizer sample			
		Blank	Ca/MgBC+NP(b)	Ca/MgBC+NP(p)	SRF
15	Yellow	0.00±0.00c	0.88±0.11a	0.58±0.11ab	0.43±0.18b
	Red	0.28±0.04c	1.40±0.14a	1.05±0.07b	0.83±0.04b
	Sandy	0.25±0.07c	1.93±0.11a	1.75±0.07a	1.33±0.18b
30	Yellow	0.33±0.11c	2.40±0.14a	2.23±0.11a	1.58±0.11b
	Red	1.90±0.14c	3.58±0.11a	3.53±0.11a	2.93±0.11b
	Sandy	1.28±0.11c	3.23±0.18a	3.10±0.14a	2.45±0.07b
45	Yellow	0.65±0.07c	3.38±0.11a	3.18±0.11a	2.73±0.18b
	Red	2.63±0.11c	6.03±0.11a	5.78±0.11a	4.95±0.07b
	Sandy	2.03±0.18c	4.30±0.14a	3.70±0.21a	2.83±0.18b
60	Yellow	0.85±0.07c	4.08±0.11a	3.53±0.18b	3.88±0.18ab
	Red	3.43±0.11c	9.03±0.11a	8.85±0.07a	6.83±0.18b
	Sandy	2.83±0.32c	5.93±0.11a	4.78±0.25b	3.18±0.25c
75	Yellow	1.23±0.18c	5.13±0.18a	4.10±0.14b	4.43±0.11b
	Red	5.83±0.25d	18.85±0.21a	17.38±0.53b	7.73±0.32c
	Sandy	3.48±0.25c	10.73±0.32a	6.78±0.39b	3.88±0.53c
90	Yellow	2.13±0.11c	10.83±0.46a	8.88±0.53ab	9.88±0.18b
	Red	6.73±0.32d	28.00±0.99a	23.80±0.42b	11.23±0.32c
	Sandy	6.60±0.21d	16.83±0.46a	12.58±0.39b	9.33±0.46c

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

Table S6 The economic evaluation for the production of Ca/MgBC + NP.

Project	Consumption	Cost (\$)
Biochar	1t	13.80–41.41
Sodium alginate (SA)	1t	165.66–276.10
CaCl ₂	1t	41.41–69.02
MgCl ₂	1t	41.41–62.12
NH ₄ Cl	1t	75.93–96.63
KH ₂ PO ₄	1t	414.15–552.20
Water	1t	0.52
	1t (grind) 40–50 kW/h	2.75–3.44
Electricity	1t (drying) 90–100 kW/h	6.19–6.88
	1t (calcine) 112–124 kW/h	7.70–8.53

Table S7 Comparison of production cost of Ca/MgBC+NP and purchase price of SRF.

Samples	Biochar	SA	CaCl ₂	MgCl ₂	NH ₄ Cl	H ₂ PO ₄	Water	EC	Cost
(t)	(t)	(t)	(t)	(t)	(t)	(t)	(t)	(kW/h)	(t/\$)
Ca/MgBC+NP	1	0.2	0.73	2.033	0.075	0.1	20	241–274	225.71–351.61
SRF	–	–	–	–	–	–	–	–	4141.47

Table S8 Composite scores and rankings of principal components.

Soil	Factor 1	Factor 2	Composite scores	Ranking
Yellow	–2.41	–4.27	–2.93	3
Red	–3.66	3.18	–0.69	2
Sandy	6.09	1.09	3.62	1

References

Li H, Wang Y, Zhao Y, Wang L, Feng J, Sun F (2023). Efficient simultaneous phosphate and ammonia adsorption using magnesium-modified biochar beads and their recovery performance. *Journal of Environmental Chemical Engineering*, 11(5): 110875 doi:10.1016/j.jece.2023.110875