Supporting information

Calcium-Modified Coal-Based Humin Waste Residue: Enhanced Cadmium Remediation in Combined Soil-Plant Systems

*Corresponding author: Zhanyong Fu
E-mail address: fzy721521@126.com

Text S1 Materials characterization

The surface micromorphological characteristics of NHM and Ca-HM were examined using scanning electron microscopy (SEM, S-4800, Japan) equipped with a cold cathode field emission electron source. Fourier-transform infrared spectroscopy (FTIR, Nicolet IS10, USA) was utilized to qualitatively analyze the functional group composition of the coal-based humic substance. Infrared spectra were acquired via the KBr pellet method, with a sample-to-KBr mass ratio of 1:160. The distribution of surface carbon atoms was analyzed using solid-state ^{13}C-CPMAS-NMR spectroscopy (AVANCE III 400 MHz, Germany). Peak deconvolution was performed using Origin 2018 software to further resolve the distribution of oxygen-containing functional groups bonded to carbon atoms. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, CA, USA) was employed to semi-quantitatively analyze the chemical states of elements in NHM and Ca-NHM before and after cadmium adsorption. Testing conditions included a resolution of 0.43 eV, an analytical chamber vacuum better than 5×10^{-10} mbar, an energy analysis range of 0–5000 eV, and a pass energy range of 1–400 eV. For zeta potential measurements, NHM and Ca-HM samples were ultrasonically dispersed, and the supernatant was analyzed using a Zeta potential analyzer (Zetasizer Nano ZS90, UK) under varying pH conditions. Acidic functional groups were quantified through Boehm titration, and the humic acid content was determined by measuring the yield of humic acids extracted from coal.

Text S2 Laboratory culture experiment

1) Different Cd pollution concentration experiment

Cd-contaminated soils were prepared at concentrations of 0, 0.2, 0.5, 1, 3, 5, 7, 10, and 20 mg/kg by homogenously mixing the materials in plastic culture cups. The soil moisture content was adjusted to 20% (w/w). The soils were then aged in a thermostatic incubator at 25℃ to achieve equilibrium and stability of cadmium (Cd) species. After 30d of incubation, soil samples were collected for determination of bioavailable Cd content.

2) NHM and Ca-NHM addition experiment

Cd-contaminated soil was prepared using a $Cd(NO_3)_2 \cdot 4H_2O$ solution. After thorough and uniform mixing, the soil was aged for 30d at 70% water holding capacity (WHC) on a dry weight basis. The measured concentration of Cd was found to be 6 $mg \cdot kg^{-1}$. Cd contaminated soil was mixed well with the materials in the proportion (0, 0.2, 0.5, 1, and 2%) into culture cups. Cultivation method as in 1.2 1).

3）Cd leaching toxicity test

Leaching Solution Preparation:①Acid leaching solution was prepared according to HJ/T300-2007 standard. ②Alkali leaching solution was prepared by adjusting the pH to 11.00±0.05 using 0.01 M NaOH.

Soil Treatment: NHM and Ca-NHM were added to the Cd-contaminated soil at 1% (w/w) application rates. After thorough mixing, the soil moisture content was adjusted to 20% (w/w) and samples were incubated at 25℃ for 7d.

Leaching Procedure: Soil samples (5.00±0.05 g) were transferred to 250 mL Erlenmeyer flasks. Then, 50 mL of either the prepared acid leaching solution (①) or alkali leaching solution (②) was added to respective flasks. The mixtures were shaken at 25°C for 48 h. The filtrate was collected in 10 mL centrifuge tubes, and Cd^{2+} concentrations were determined by ICP-MS.

Text S3 Cadmium bioefficacy evaluation model

To assess the biological availability of Cd in soils, the following equations provided by Wen et al. (2020) were used to calculate passivation efficiency (η), activity coefficient (k), and the ratio of activity to stability (h):

The passivation efficiency(η, %) calculation formula as follows:

$$\eta = \frac{(A_1 - A_2)/A_1 + (A_3 - A_4)/A_4}{2} \times 100\%$$

Where A_1 and A_4 are respectively acid extraction and residue content of Cd in soil without coal-based humin ($mg \cdot kg^{-1}$); Where A_2 and A_3 are respectively acid extraction and residue content of Cd in soil supplemented coal-based humin ($mg \cdot kg^{-1}$)

Activity coefficient (k) reflects the difficulty of absorption of cadmium in soil by pakchoi. The calculation formula as follows:

$$k = \frac{f_1}{f_1 + f_2 + f_3 + f_4}$$

The ratio of activity to stability (h) reflects the risk of Cd release in soils. The calculation formula as follows:

$$h = \frac{f_1}{f_4}$$

Where f_1, f_2, f_3 and f_4 are the contents of acid-extracted cadmium, reduced cadmium, oxidized cadmium and residual cadmium of soil samples under different treatments, respectively.

Text S4 Cadmium ecological effect evaluation model

The ratio of secondary phase to primary phase (RSP) method evaluates cadmium's ecological effects by analyzing its chemical speciation, reflecting its environmental chemical activity (Zhao et al., 2013). As detailed in Table S1, higher K_{RSP} values indicate greater cadmium enrichment and elevated pollution levels. The calculation formula is as follows:

$$K_{RSP} = \frac{F_{sec}}{F_{prim}}$$

K_{RSP} represented the distribution ratio of cadmium between secondary and primary phases in differently treated soil samples, F_{sec} and F_{prim} denoted the cadmium concentrations in the secondary and primary phases, respectively.

Table S1 Relationship between K_{RSP} value and pollution degree

K_{RSP}	<1	1-2	2-3	≥3
Pollution level	No pollution	Slightly-polluted	Moderate pollution	Severe pollution

Text S5 Cadmium ecological risk assessment model

The Risk Assessment Code (RAC) was primarily used for environmental risk assessment of heavy metals by analyzing their bioavailable fractions in soils (Zhang et al.,2022; Huang et al.,2019). As shown in Table S2, the ecological risk classification

demonstrated that higher RAC values correspond to greater environmental risks from heavy metals. The calculation formula was as follows:

$$RAC = \frac{A_1 + B_1}{M} \times 100\%$$

RAC was Ecological Risk Assessment Index, A_1 was Exchangeable cadmium content in soil (mg/kg), B_1 was Carbonate-bound cadmium content in soil (mg/kg), M was Total heavy metal content (mg/kg).

Table S2 Ecological risk classification level

RAC	<1%	1-10%	11-30%	31-50%	>50%
Ecological risk classification	Safety	Low risk	Medium risk	High risk	Ultra-high risk

Text S6 Plant-soil system cadmium transport modeling

The Cd concentration in shoot, the bioconcentration factor (BCF), the translocation factor (TF) and the resistance coefficient defined as transferability of Cd from soil to pakchoi were calculated as below (Abid et al., 2025; Daryabeigi et al., 2022; Rosca et al., 2021):

$$\text{Cd concentration in shoots} = \text{Cd concentration in shoots} \times \text{Shoots biomass}$$

$$BCF = \frac{\text{Cd concentration in shoots}}{\text{Cd concentration in soil}}$$

$$TF = \frac{\text{Cd concentration in shoots}}{\text{Cd concentration in roots}}$$

$$\text{Resistance coefficient} = \frac{\text{total biomass of pakchoi with NHM and Ca - NHM}}{\text{total biomass of pakchoi with CK}}$$

Table S3 Orthogonal experiment design-factors and levels

	A	B	C
	Ratio of NHM: $Ca(OH)_2$	Hydrothermal temperature（℃）	Ultrasound time（h）
1	3:1	25	1
2	3:2	55	3
3	3:3	85	5

Table S4 Orthogonal table

	A	B	C
	Ratio of NHM: $Ca(OH)_2$	Hydrothermal temperature（℃）	Ultrasound time（h）
CK	-	-	-
1	A1	B1	C1
2	A1	B2	C2
3	A1	B3	C3
4	A2	B1	C2
5	A2	B2	C3
6	A2	B3	C1
7	A3	B1	C3
8	A3	B2	C1
9	A3	B3	C2

Table S5 Test of influence of three factors on adsorption capacity of calcified modified NHM

Source	Type III sum of squares	Degree of freedom	Mean square	F	Sig significance
Modified model	6.264[a]	6	1.044	16.202	0.059
Intercept	23201.382	1	23201.382	360083.534	0.000
A	3.882	2	1.941	30.123	0.032
B	2.154	2	1.077	16.717	0.056
C	0.227	2	0.114	1.765	0.362
Error	0.129	2	0.064		
Total	23207.775	9			
Total after correction	6.329	8			

a. R^2=0.980（After adjustment R^2=0.919）

Note : The significance level is 0.10.

Table S6 The change of the exchangeable calcium content of NCH and Ca-NCH before and after adsorption

Samples	NHM	Ca-NHM	NHM-Cd	Ca-NHM-Cd
exchangeable calcium (g/kg)	2.97	16.22	0.68	5.50

Table S7 Relative proportion of main functional groups of coal-based humin

Samples	Chemical shift(ppm) and carbon assignment(%)					Aliphatic	Polar	Aromatic
	0-50	50-100	100-145	145-163	163-200	C(%)[a]	C(%)[b]	polar C(%)[c]
NHM	44.61	7.36	26.49	2.21	19.33	51.97	24.69	17.33
Ca-NHM	42.10	10.50	27.11	4.30	15.99	52.60	30.79	20.29

[a] Aliphatic C(%): total aliphatic C region(0-100ppm)

[b] Polar C(%); toal polar carbon regin(50-100 and 145-200ppm)

[c] Aromatic polar C(%): toal polar carbon region(145-200ppm)

Table S8 K_{RSP} values of heavy metals and changes of ecological risk index

Treatment	CK	NHM	Ca-NHM
K_{RSP}	8.63±0.21a	6.81±0.84b	5.93±0.44b
RAC(%)	52.83±0.95	51.53±0.82	49.85±0.55

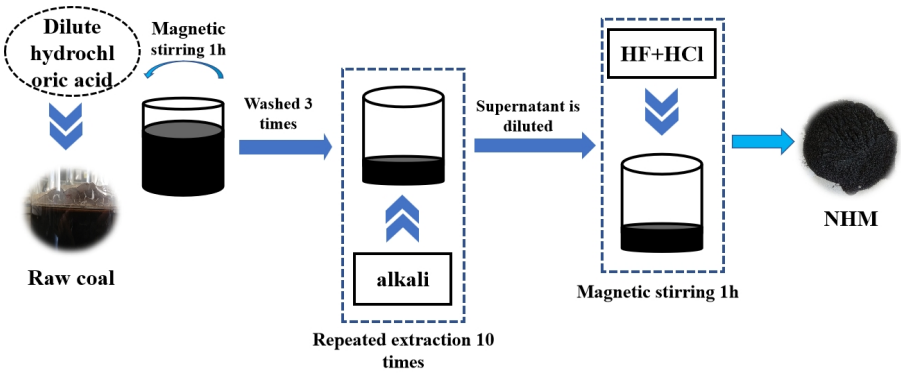


Figure S1 Extraction process of NHM

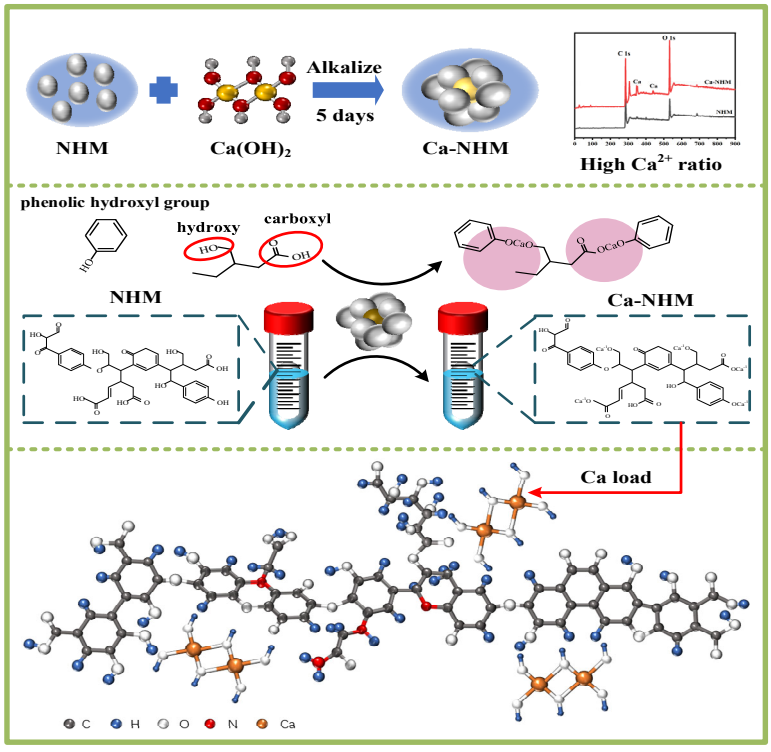


Figure S2 Calcium-based humin preparation

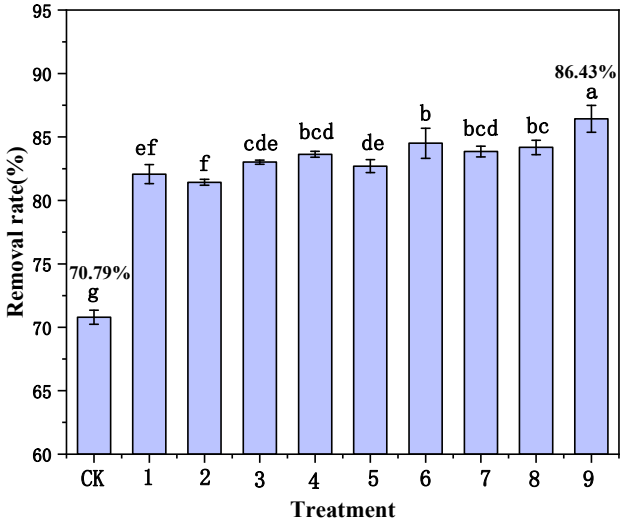


Figure S3 Cadmium removal rate of humin prepared under different conditions

References:

58. Wen X., Gu J., ,Wei C., *et al*. Preparation of humic acid-sepiolite composite passivator andits remediation effect on Cd contaminated soil. Environmental Protection of Chemical Industry, 2020, 40(05): 518-523.

59. Zhang Z.G., Cai W.Q., Hu Y.B., et al. Ecological risk assessment and influencing factors of heavy-metal leaching from coal-based solid waste fly ash. Frontiers in Chemistry, 2022, 10: 932133.

60. Huang Y., Wang M.X., LI Z.J., *et al*. In situ remediation of mercury-contaminated soil using thiol-functionalized graphene oxide/Fe-Mn composite. Journal of Hazardous Materials, 2019, 373: 783-790.

61. Zhao S., Li C., Shi X., *et al*. Bioavailability and environment pollution evaliation of sediments heavy metals in wuliangsuhai lake. Ecology and Environmrntal Science, 2013, 22(3): 481-489.

62. Daryabeigi A., Muhling K.H. Phytoremediation capability and copper uptake of maize (Zea mays L.) in copper contaminated soils Pollut, 2022, 2(1) : 53-65,

63. Rosca M., Cozma P., Minut M., *et al*. New evidence of model Crop Brassica napus L. in soil clean-up: comparison of tolerance and accumulation of lead and cadmium Plants, 2021, 10 (10): 2051.

64. Abid H., Mahroof S., Ahmad K.S., *et al*. Harnessing native plants for sustainable heavy metal phytoremediation in crushing industry soils of Muzaffarabad. Environmental Technology & Innovation, 2025, 38: 04141.

65. HJ/T300-2007 standard