Supplementary Materials of the manuscript:

Towards engineering mitigation of leaching of Cd and Pb in co-contaminated soils using metal oxide-based aerogel composites and biochar

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Experimental Section

Materials: All chemicals applied in this study, including Iron (III) nitrate nonahydrate (Fe (NO3)3 · 9H2O), Manganese (II) nitrate tetra-hydrate (Mn (NO3)2 · 4H2O), Strontium nitrate (Sr (NO3)2), Cobalt (II) nitrate hexahydrate (Co (NO3)2 · 6H2O), Citric acid (C6H8O7), and Ethylene-diamine-tetra-acetic acid (EDTA) for synthesized metal oxides; Resorcinol (C6H6O2), Formaldehyde (H2CO) and Sodium carbonate (Na2CO3) for preparing Carbon Aerogel, and NaOH, Acetic Acid, Hydrogen Proxide, Nitric Acid, Hydroxylamine hydrochloride were of analytical grade and purchased from Sigma Aldrich. All chemicals used without further purification.

loss-on–ignition method: After passing through a 2-mm sieve, soil samples were dried in oven-dried a 105° C overnight. Then, samples were cooled in a desiccator, and weighed before they were combusted at 300, 360, 400, 500, and 550° C for 2 h in a muffle furnace. After cooling samples in a desiccator and weighed again, an estimation of soil organic matter percentage was calculated.

Cation exchange capacity (CEC) using BaCl$_2$. The 2.5 g of samples is saturated in 30 ml of 0.1 mol L^{-1} BaCl$_2$ solution and shaken for 1 hour. After separating solid and liquid phases repeated three times by centrifugation, the supernatant exchangeable ions (potassium, sodium, magnesium, and calcium) were measured by ICP-OES. Soil residuals was treated with 30 ml of 0.0025 mol L^{-1} BaCl$_2$ and shaken for 24 hours. The supernatant liquid obtained from separation solid phase was decant and solid mass was weighed. Nearly 30 ml 0.02 mol L^{-1} MgSO$_4$ was added to solid phases and mixture was shaken overnight. After separating of supernatant liquid from solid phases through filter paper, the CEC of liquid solution was measured.

Preparation of Amendments: Carbon aerogel (CAg) was synthesized with a resorcinol-formaldehyde (R/F) as precursor sources and Na$_2$CO$_3$ as basic catalyst. About 0.29 moles Resorcinol was dissolved in 100 ml of distilled water. The formaldehyde solution was added to the Resorcinol solution (R/F = 0.5 molar ratio) and stirring on a mechanical shaker (Heidolph Instruments, Unimax 2010) with rotation speed of 150 rpm for 10 min. Then, a 0.1 M aqueous solution of sodium carbonate was added to Resorcinol/Formaldehyde solution and stirred under nitrogen atmosphere for nearly 30 min.   Next, it

was hold in a vacuum oven (70° C) for 7 days to get aerogel, following keeping in acetic acid (3% wt.) for 1 day, then replacement with tert-butanol for 3 days, and afterwards, the freeze-drying process (FD-1-50, Boyikang Laboratory Apparatus Co., Ltd., Beijing, China) was performed to get the final product. The carbon aerogel was placed in a tubular furnace (GSL-1700X, MTI Corporation, USA) at a temperature of 800° C (a ramping rate of 5°C/min) under N_2 flow (120 ml min^{-1}) to get carbonized CAg. Biochar was prepared from coconut coil fiber as precursor's material. Coconut Fibers was separated from the shell of coconuts, grounded and dried at 60^0 C in the vacuum oven overnight. Afterwards, it activated and heated at 1000^0 C under atmosphere of CO_2 (flow rate of 200 ml min^{-1}) and hold for 3h.

Mixed metal oxides were considered as an effective agent with chelating (or complexing) features in immobilization and stability heavy metals in the soils. The salt nitrates of strontium, manganese, cobalt, and iron (that showed as $Sr_{0.7} Mn_{0.3} Co_{0.5} Fe_{0.5}O_3$) were applied for mixed metal oxides as precursor's materials. $Sr_{0.7} Mn_{0.3} Co_{0.5} Fe_{0.5}O_3$ is synthesized with an effective method that used from EDTA and Citric Acid (CA) as complexing agents to chelate metals together. Briefly, the nitrate of Strontium (3.7 g), Manganese (1.88 g), Iron (5.05 g), and Cobalt (3.6 g) were added each in 25 mL deionized water and stirred on the mechanical shaker for 1 hour. After completely dissolved, the citric acid (CA) and ethylene diamine tetra-acetic acid (EDTA) with molar ratio of 1.2/1/1 (CA/EDTA/total metal ions) were slowly pouted to solution. Then to form clearly gel, the mixed solution was stirred at 95^0 C for 3 hours and then dried at vacuum oven overnight. For pH adjustment, the ammonia solution 1 M was applied. Final, the formed gel was activated in a tube furnace firstly at 450^0 C and then 800^0 C for 8 and 7 hours, respectively. The result metal oxide was kept in the desiccator for following tests.

Metal oxides/CAg was prepared by adding them in 100 ml distilled water and stirred to completely mix. Then sodium hydroxide at two steps was added to prepared solution; firstly, adding gradually 140 mL of 1.5 mol L^{-1} NaOH and letter is adding slowly 100 mL of 3 mol L^{-1} during 1 hours and then stirred vigorously at room temperature for 24 and 12 hours, respectively. The result solution was centrifuged and filtered to obtain solid matters and then washed several time using distilled water to remove impurities and achieving the pH = 7-8.

TCLP test: the Toxicity characteristic leaching procedure (TCLP) was performed to realize the behavior of mobility and also immobilization performance of Cd (II) and Pb (II) in co-contaminated soils. The 40 ml TCLP extraction solution was used to extract process of 2 g soil in pH less than of 5. The obtained mixture was mixed on a shaker for 16 h at 250 rpm and then centrifuged and filtered through a Millipore filter (0.45 μm) and then analyzed with ICP-OES (iCAP 6500, Thermo Fisher Scientific) to measure mobilized Cd (II) and Pb (II).

Leaching test. The experiments of leaching were carried out by pouring roughly 200 mL distilled water over each pot every 7 days. The heavy metal concentrations were analyzed after sampling leachate from bottom of the pot and the pH measurement. Preserving of samples for elemental analysis was conducted by adding few droplets of HNO_3 into each vial. Cadmium, lead, and chromium were measured by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES) (iCAP 6500, Thermo Fisher Scientific).

Plant (bio) availability of Pb (II) and Cd (II). The plant availability of Cd (II) and Pb (II) in amended-soil was investigated after extraction with DTPA/TEA (pH 7.3). the resulted solution analyzed for Cd (II) and Pb (II) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Co., USA).

Extraction of soil heavy metals with CaCl2 and aqua regia: The heavy metals concentration in the pore-water was measured by ICP-OES after extraction with the $CaCl_2$ (0.01 mol L^{-1}). Generally, take samples from each pot and then dried completely in oven at 50° C. a 5g dried samples each pot was separately mixed by 25 mL of $CaCl_2$ and agitated for 2 hours. Afterwards, samples were withdrawn, centrifuged, and filtered. The filtrate samples were kept at 4° C in refrigerators after adding one or two drops HNO_3.

Pseudo-Total metal content that indicates the eco-toxicological impacts of heavy metals burden in soil was measured by digestion with aqua regia. Briefly, 2g dried samples was mixed by 40 mL HCl / HNO_3 mixture (3:1 % V/V). The suspension was digested at room temperature for 15 h under hood, and then

was digested at 130 ˚C for 2 h under reflux conditions. After to cool down room temperature and diluted to 100 mL 0.5 mol L^{-1} HNO$_3$, and stored at 4˚C for analysis.

Sequential extraction: The evaluation and comparison of various amendments on Metal distribution and mobility in soil was applied using sequential extraction that proposed by BCR:

Step 1. 1 g of samples was added to 40 mL of 0.11 mol L^{-1} Acetic Acid under shaker condition for overnight at room temperature. After that, the extraction suspension was centrifuged for 20 min to separate solid samples from the extract. Then the extract kept at 4˚ C for analysis after adding two or three drops of nitric acid. The solid samples were immersed with distilled water for 20 min under a mechanical shaker, then centrifuged, the solution discarded and solid dried in the oven to the next step.

Step 2. The residue from step 1 was mixed by 40 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride and the extraction procedure was applied as described above.

Step 3. The extract agent in this step was 8.8 mol L^{-1} hydrogen peroxide (10 mL) that added to the residue sample from step2. Firstly, the vessels were covered and digested for 1 h at room temperature with sometimes manual shaking. Later, the digestion was continued by putting vessels in a water bath (90˚ C) for 1 h until the volume of vessels reduced to less than 3 ml by additional heating of vessel. Then, a second hydrogen peroxide solution (10 mL) was added and the procedure was conducted again as described above. A 1 mol L^{-1} of Ammonium acetate (50 mL) was added to moist residue that adjusted to pH 2 with HNO$_3$. The solution was shaken, centrifuged and separated as described in step 1.

Step 4. To determine the fraction bound to carbonate bound of influences soil with treated amendments, a 1 mol L^{-1} Sodium acetate (25 mL) adjusted at pH 5 was added the residue sample from step 3. The extraction procedure is the same as step 1.

Supplementary Tables

Table S1. Physicochemical properties of soil and amendments used in the experiment.

Property	Soil	CCFB	CAg	MO-CAg
pH	7.98	9.5	8.5	8.2
Ash (%)	-	22.52	16.7	11.87
EC (ds.m^{-1})	0.21	0.16	3.25	2.92
Organic matter (g kg^{-1})	62.33	820.21	735.01	550.4
AP (mg kg^{-1})	33.45	42.25	57.11	51.23
TK (g kg^{-1})	21.55	5.67	14.23	11.78
TOC (g kg^{-1})	36.16	475.44	511.92	497.36
Total pore volume (cm^3 g^{-1})	-	1.22	1.06	1.12
BET (m^2 g^{-1})	0.69	856	714.93	759.52
Moisture (%)	17.95	8.23	18.2	14.25

[a] electrical conductivity;
[b] Brunauer-Emmett-Teller surface area;
[c] Mean ± standard.

Table S2: Influence of the studied amendments on soil properties.

Variables	DOC (mg kg^{-1})	SOM (mg kg^{-1})	pH	CEC (cmol kg^{-1})
Control	0.18	38.43	8.34	21.50
CCFB	0.36	51.01	8.38	16.32
CAg	0.42	56.74	8.37	15.12
MO-CAg	0.38	45.27	8.30	16.14
MO	0.34	40.90	3.69	15.83

SOM=Soil organic matter;
CEC= Cation exchange capacity.

Table S3. The Brunauer-Emmett-Teller (BET) surface area analysis and pore volume of synthesized materials

Catalysts	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Mean pore diameter (nm)
CAg	714.93	1.06	6.15
CCFB	856	1.22	2.4
MO-CAg	759.52	1.12	11.51

Table S4. Obtained zeta potential (mV) of prepared materials before and after adsorption

Samples	Zeta potential (mV)	
Before adsorption		
CAg	-48.1 ± 1.7	
CCFB	-39.2 ± 1.2	
MO-CAg	-24.4 ± 1.3	
After adsorption	**Pb (II)**	**Cd (II)**
CAg	-18.6 ± 0.09	-22.02 ± 1.3
CCFB	-25.20 ± 1.1	-28.82 ± 1.2
MO-CAg	-16.32 ± 0.08	-12.58 ± 0.07

Table S5. Probable bonding between heavy metals and materials in co-contaminated soils

| Material	Rank	Bond	d [Å]	d-Ratio
CCFB	1	Pb-O	1.5195	0.9045
	2	Pb-O	1.5232	0.9066
	3	Pb-O	1.5348	0.9129
	4	Cd-O	2.5306	1.5086
	5	Cd-O	2.5411	1.5125
	6	Cd-O	2.6102	1.6155
CAg	1	Pb-O	1.3581	0.7073
	2	Pb-O	1.3721	0.7514
	3	Pb-O	1.3889	0.7823
	4	Cd-O	1.4124	0.8015
	5	Cd-O	1.4239	0.8107
	6	Cd-O	1.4301	0.8291
MO-CAg	1	Pb-Fe-O	1.1226	0.6449
	2	Pb-Co-O	1.9556	1.1175
	3	Pb-Mn-O	2.3422	0.9257
	4	Cd-Fe-O	0.8226	0.4329
	5	Cd-Co-O	1.8476	1.0550
	6	Cd-Mn-O	2.2862	0.9036

Supplementary Figures
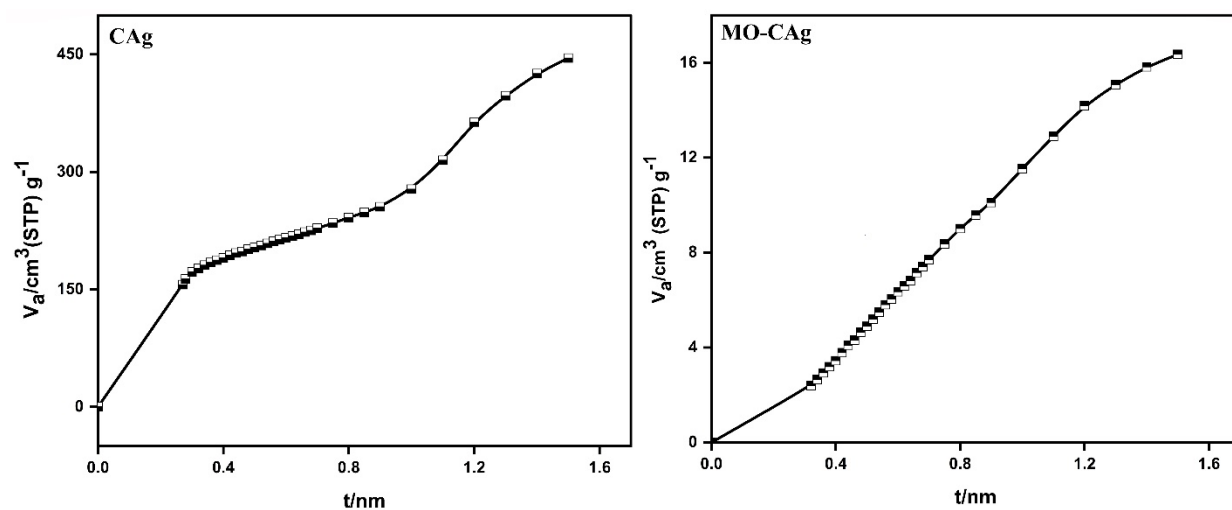
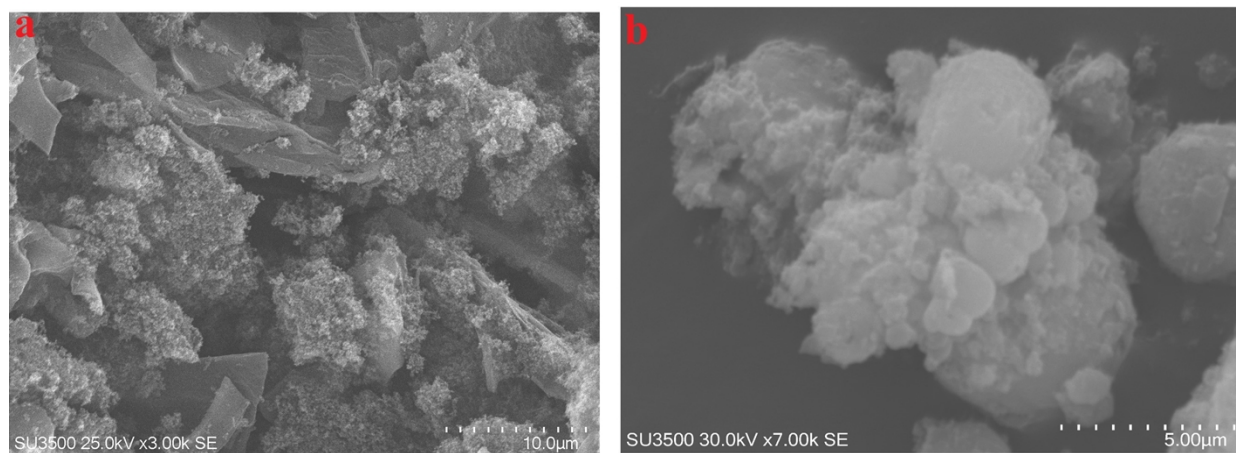**Figure S1.** The V-t curve of CAg and MO-CAg obtained from BET analysis

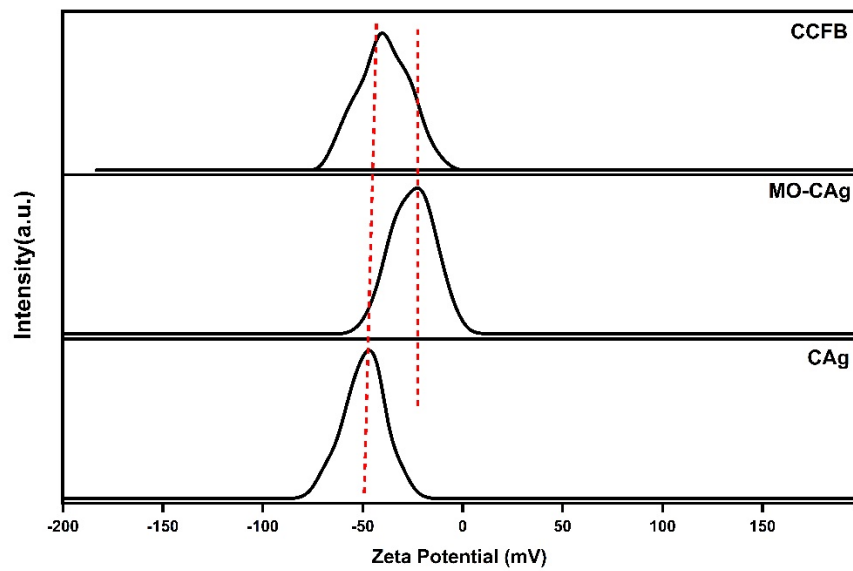
Figure S2. The SEM images of (a) CCFB; and (b) MO-CAg

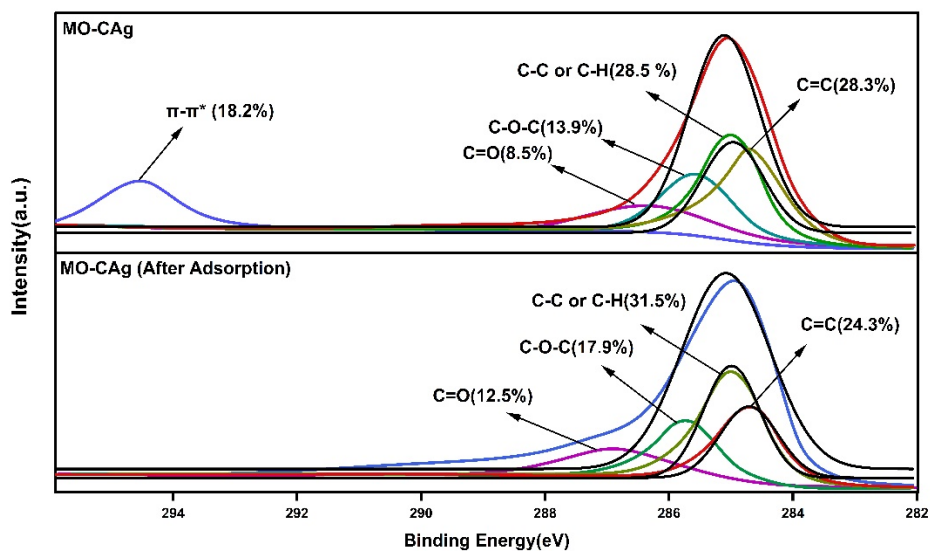**Figure S3:** Behavior of synthesized materials in terms of zeta potential

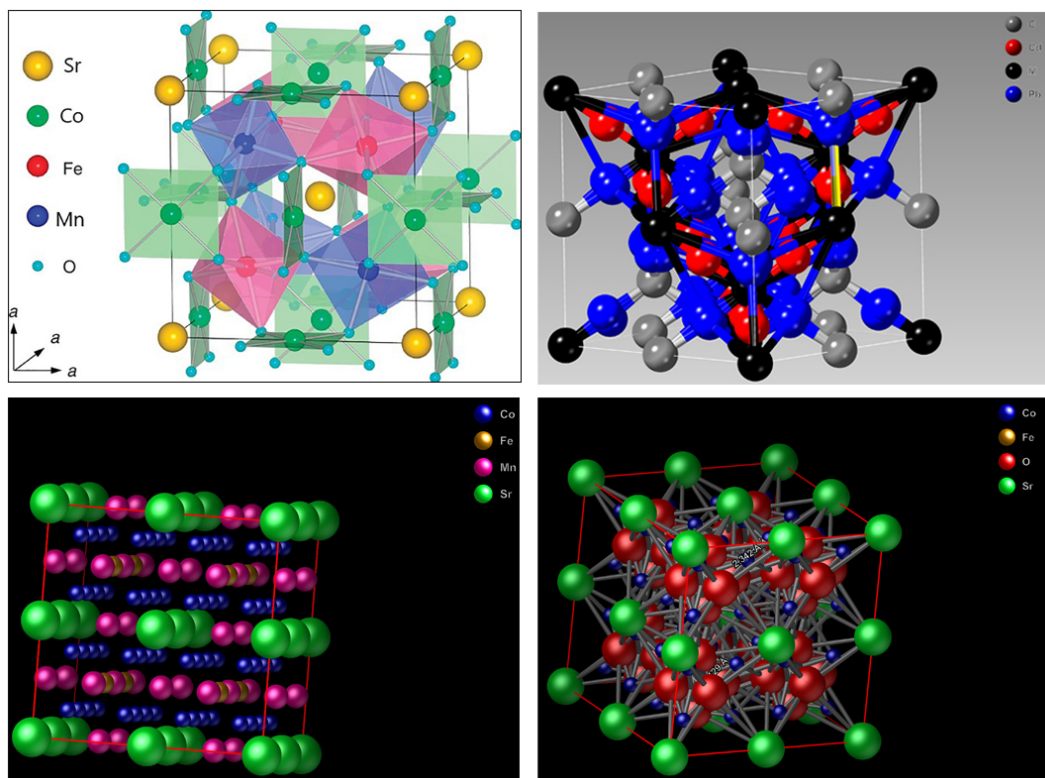**Figure S4:** C 1s XPS of MO-CAg Before and after adsorption

Figure S5. Atomic configuration of probable bonding of MO-CAg

References

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