

Supporting Information for

Simulated Environmental Aging Increases Cadmium Extractability in Acidic Soil Amended with Cadmium- Containing Rice-Straw Biochar

Xianxiang Li ^{1,2,3}, Yuchao Fan ^{1,2,3}, Hongbiao Cui ^{1,2,3,*}, Liya Liu ^{1,2,3}, Ruizhi Xia ⁴, Lijun Zhou ^{5,*}, Qiugang Wu ¹, Jun Zhou ⁴

¹ Anhui Province Engineering Research Center of Water and Soil Resources Comprehensive Utilization and Ecological Protection in High Groundwater Mining Area, Anhui University of Science and Technology, Huainan 232001, China

² State Key Laboratory for Safe Mining of Deep Coal Resources and Environment Protection, Huainan 232000, China

³ School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China

⁴ Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy Sciences, Nanjing 211135, China

⁵ Jiangxi Institute of Red Soil and Germplasm Resources, Nanchang 331717, China

** Corresponding authors*

E-mail addresses: hbcui@aust.edu.cn (H. C.) and huoe861200@163.com (L. Z.).

Text S1. Characterization of biochar for analytical determination of parameters

The specific surface area (SSA) and porosity was determined using the N₂ adsorption-desorption isotherm of a specific surface area analyzer (Micromeritics ASPA 2460 Version 2.02) at 77 K and a relative pressure P/P_0 of 0.1 and calculated using Brunauer Emmet and Teller (BET) theory. The particle structure and surface morphology of the biochar were determined using field emission scanning electron microscopy (SEM Quanta 400 FEG, FEI, USA) before and after composite aging. A Fourier Transform infrared spectrometer (FTIR) (Nicolet IS50, Thermo, USA) was used to determine the surface functional groups of the biochar with a scanning range of 4000-500 cm⁻¹ and a resolution of 2 cm⁻¹. Raman spectroscopy was performed using Horiba LabRam HR800 Evolution spectrometer with a 532-nm red monochromator as laser excitation source. The compositions of oxygen- and carbon-containing functional groups on the surface of biochar were determined by XPS using an X-ray photoelectron spectrometer (ESCALAB Xi⁺, Thermo Fisher Scientific, USA) with a full-spectrum scanning energy range of 0-1200 eV in steps of 1 eV and a fluence energy of 100.0 eV, and the spectra were analyzed using Avantage. The crystalline components of biochar were determined using a Biochar XRD Analytical Ultima IV Combined Multifunctional Horizontal X-ray Diffractometer (Rigaku Smartlab, Japan) with a scanning step of 0.02 ° and a scanning speed of 2 °·min⁻¹.

Table S1 The detailed cycle count and sampling schedule for the CB treatment

Accelerated simulated aging level	Number of Accelerated Simulated Aging Cycles				Replicates	Sampling Time Points
	DW cycles	FT cycles	fertilizer application	acid rain		
Accelerated simulated aging equivalent to 0 year	0	0	0	0	3	0 day
Accelerated simulated aging equivalent to 1 year	5	2	1	1	3	7th day
Accelerated simulated aging equivalent to 4 years	20	8	4	4	3	28th day
Accelerated simulated aging equivalent to 8 years	40	16	8	8	3	56th day

Table S2 Specific surface area and porosity of biochars before and after the accelerated simulated aging

Biochar	Specific surface area (m ² ·g ⁻¹)	Total hole capacity (cm ³ ·g ⁻¹)	Average pore size (nm)
CB-0	4.93	0.0209	17.0
CB-1	4.14	0.0186	18.0
CB-8	6.99	0.0235	13.4
PB-0	5.72	0.0173	12.1
PB-1	4.72	0.0194	16.4
PB-8	5.98	0.0219	14.6

Table S3 Two-way ANOVA test showing F-value of parameters of biochar affected by biochar types (BC: CB and PB) and simulated aging years (SY: 0, 1, 4, and 8 years).

Source of Variation	df	pH		Water-soluble Cd		CaCl ₂ extractable Cd	
		F-value	<i>p</i> -value	F-value	<i>p</i> -value	F-value	<i>p</i> -value
BC	1	4.34 ^{ns}	0.054	233.13 ^{***}	< 0.001	550.38 ^{***}	< 0.001
SY	3	4446.06 ^{***}	< 0.001	346.61 ^{***}	< 0.001	392.45 ^{***}	< 0.001
BC × SY	3	32.79 ^{***}	< 0.001	5.74 ^{***}	< 0.001	3.07 ^{ns}	0.058
Error	12	-	-	-	-	-	-

Notes: ns indicates that there is no significant difference, $p > 0.05$.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Table S4 The chemical fractions of endogenous Cd ($\mu\text{g}\cdot\text{kg}^{-1}$) in biochars

Treatments	F1	F2	F3	F4	Total Cd
CB-0	886.9 $\pm$ 14.1aB	2204.4 $\pm$ 13.9dB	1772.4 $\pm$ 72.5aB	648.1 $\pm$ 35.5bB	5511.8 $\pm$ 273.1bB
CB-1	641.3 $\pm$ 27.2bB	3041.6 $\pm$ 109.6cB	1405.7 $\pm$ 34.1bA	628.9 $\pm$ 35.4bB	5717.5 $\pm$ 153.9bB
CB-4	649.3 $\pm$ 40.6bB	3483.7 $\pm$ 116.9bB	944.3 $\pm$ 24.4cB	613.4 $\pm$ 26.3bB	5490.5 $\pm$ 224.8bB
CB-8	424.9 $\pm$ 24.9cB	3808.3 $\pm$ 153.9aB	730.8 $\pm$ 38.9dB	633.7 $\pm$ 34.7bB	5586.9 $\pm$ 368.1bB
PB-0	1257.1 $\pm$ 30.9aA	2653.2 $\pm$ 33.2cA	2157.4 $\pm$ 96.6aA	2219.5 $\pm$ 102.3aA	8287.1 $\pm$ 150.9aA
PB-1	985.4 $\pm$ 32.5bA	4006.2 $\pm$ 242.3bA	1369.7 $\pm$ 191.8bA	1639.8 $\pm$ 315.7aA	8001.12 $\pm$ 97.4aA
PB-4	891.5 $\pm$ 24.1bcA	4402.4 $\pm$ 140.3aA	1210.3 $\pm$ 118.1bA	1635.4 $\pm$ 440.3aA	8139.5 $\pm$ 266.5aA
PB-8	780.8 $\pm$ 75.7cA	4490.9 $\pm$ 75.0aA	1090.5 $\pm$ 52.8bA	1875.0 $\pm$ 96.8aA	8237.2 $\pm$ 39.0aA

Note: The values in the table are expressed as mean $\pm$ standard deviation. Different lower-case letters indicate a significant difference between experimental groups with the same biochar type ($p < 0.05$), while the different capital letters indicate a significant difference between experimental groups with the same aging time ($p < 0.05$). CB-0, 1, 4, 8 represent CB incubated for accelerated simulated aging equivalent to 1, 4, and 8 years, respectively. Similarly, PB-0, 1, 4, 8 represent PB was sampled for chemical analysis at the same time intervals (accelerated simulated aging equivalent to 1, 4, and 8 years). F1, acid-soluble fraction; F2, reducible fraction; F3, oxidizable fraction; F4, residual fraction.

Table S5 Two-way ANOVA test showing F-value of F1, F2, F3, F4 of biochars affected by biochar types (BC: CB and PB) and simulated aging years (SY: 0, 1, 4, and 8 years).

Source of Variation	df	F1		F2		F3		F4	
		F-value	p-value	F-value	p-value	F-value	p-value	F-value	p-value
BC	1	448.62***	< 0.001	202.43***	< 0.001	39.94***	< 0.001	101.07***	< 0.001
SY	3	157.01***	< 0.001	209.76***	< 0.001	144.84***	< 0.001	2.96	0.064
BC × SY	3	3.53*	0.039	5.04*	0.012	6.29**	0.005	3.35*	0.046
Error	12	-	-	-	-	-	-	-	-

Notes: * $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Table S6 Two-way ANOVA test showing F-value of parameters of soil affected by biochar types (BC: CK, CBS, and PBS) and simulated aging years (SY: 0, 1, 4, and 8 years).

Source of Variation	df	pH		water-soluble Cd		CaCl ₂ extractable Cd	
		F-value	<i>p</i> -value	F-value	<i>p</i> -value	F-value	<i>p</i> -value
BC	2	716.74***	< 0.001	660.77***	< 0.001	300.39***	< 0.001
SY	3	5116.33***	< 0.001	1701.88***	< 0.001	588.37***	< 0.001
BC × SY	6	211.59***	< 0.001	211.23***	< 0.001	85.73***	< 0.001
Error	24	-	-	-	-	-	-

Notes: * $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Table S7 The chemical fractions of Cd ($\mu\text{g}\cdot\text{kg}^{-1}$) in biochar amended soil

Treatments	F1	F2	F3	F4	Total Cd
CK-0	160.0 $\pm$ 6.37aC	18.8 $\pm$ 1.05bC	35.7 $\pm$ 1.13aC	143.1 $\pm$ 2.42abB	357.6 $\pm$ 5.95cC
CK-1	153.4 $\pm$ 4.43aC	25.3 $\pm$ 1.17aB	34.3 $\pm$ 0.43abC	135.0 $\pm$ 2.87bB	347.93 $\pm$ 6.25cC
CK-4	142.5 $\pm$ 3.61aC	26.5 $\pm$ 1.82aC	33.8 $\pm$ 1.37abC	151.0 $\pm$ 9.7abA	353.88 $\pm$ 6.22cC
CK-8	130.3 $\pm$ 4.67aC	29.1 $\pm$ 0.91aC	32.4 $\pm$ 0.57bB	156.1 $\pm$ 3.62aA	347.83 $\pm$ 6.35cC
CBS-0	354.0 $\pm$ 5.88aB	38.4 $\pm$ 5.32dB	92.7 $\pm$ 3.88aB	169.2 $\pm$ 6.64aA	654.27 $\pm$ 9.24bB
CBS-1	305.4 $\pm$ 12.8bB	74.6 $\pm$ 4.09cA	59.8 $\pm$ 5.26bB	209.3 $\pm$ 2.95aA	649.05 $\pm$ 14.59bB
CBS-4	289.2 $\pm$ 15.1bB	106.8 $\pm$ 8.07bB	58.3 $\pm$ 6.08bB	193.9 $\pm$ 32.1aA	648.15 $\pm$ 10.18bB
CBS-8	268.9 $\pm$ 19.6bB	170.6 $\pm$ 7.06aB	42.6 $\pm$ 3.71cAB	172.9 $\pm$ 7.23aA	655.05 $\pm$ 10.72bB
PBS-0	425.7 $\pm$ 8.2aA	53.2 $\pm$ 3.01dA	128.9 $\pm$ 3.34aA	177.5 $\pm$ 12.2aA	785.36 $\pm$ 14.86aA
PBS-1	410.7 $\pm$ 28.3aA	74.6 $\pm$ 5.09cA	114.6 $\pm$ 4.81abA	185.5 $\pm$ 25.4aA	785.5 $\pm$ 30.15aA
PBS-4	376.8 $\pm$ 1.72aA	147.1 $\pm$ 2.95bA	90.4 $\pm$ 10.5bA	173.5 $\pm$ 10.8aA	787.75 $\pm$ 2.48aA
PBS-8	364.8 $\pm$ 27.5aA	191.8 $\pm$ 3.53aA	60.5 $\pm$ 11.3cA	162.4 $\pm$ 29.2aA	779.47 $\pm$ 17.3aA

Note: The values in the table are expressed as mean $\pm$ standard deviation. Different lower-case letters indicate a significant difference between experimental groups with the same biochar type ($p < 0.05$), while the different capital letters indicate a significant difference between experimental groups with the same aging time ($p < 0.05$). CK-0, 1, 4, 8 represent control soil samples incubated for accelerated simulated aging equivalent to 1, 4, and 8 years treatments, respectively. Similarly, CBS-0, 1, 4, 8 and PBS-0, 1, 4, 8 represent soils amended with CB and PB that were sampled for chemical analysis at the same time intervals (accelerated simulated aging equivalent to 1, 4, and 8 years). F1: acid-soluble fraction; F2: reducible fraction; F3: oxidizable fraction, F4: residual fraction.

Table S8 Two-way ANOVA test showing F-value of F1, F2, F3, F4 of biochar-amended soils affected by biochar types (BC: CK, CB, and PB) and simulated aging years (SY: 0, 1, 4, and 8 years).

Source of Variation	df	F1		F2		F3		F4	
		F-value	p-value	F-value	p-value	F-value	p-value	F-value	p-value
BC	2	597.55***	< 0.001	1010.24***	< 0.001	273.02***	< 0.001	13.48***	< 0.001
SY	3	18.41***	< 0.001	546.62***	< 0.001	56.30***	< 0.001	1.05 ^{ns}	0.391
BC × SY	6	1.70 ^{ns}	0.165	119.46***	< 0.001	15.68***	< 0.001	1.58 ^{ns}	0.195
Error	24	-	-	-	-	-	-	-	-

Notes: ns indicates that there is no significant difference, $p > 0.05$.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Fig. S1 The process of annual accelerated simulated aging

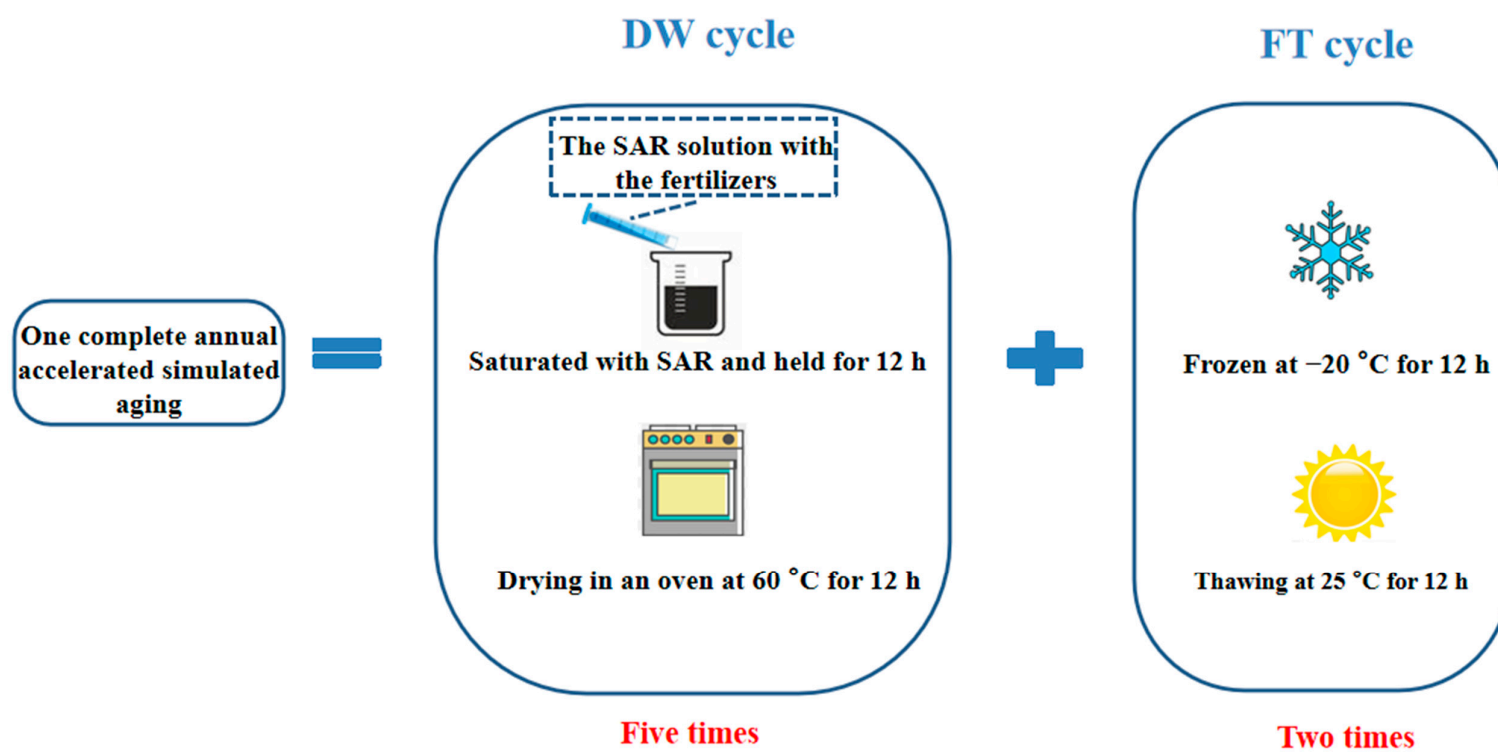


Fig. S2 The destructively sampling process for the single biochar (CB) accelerated simulated aging

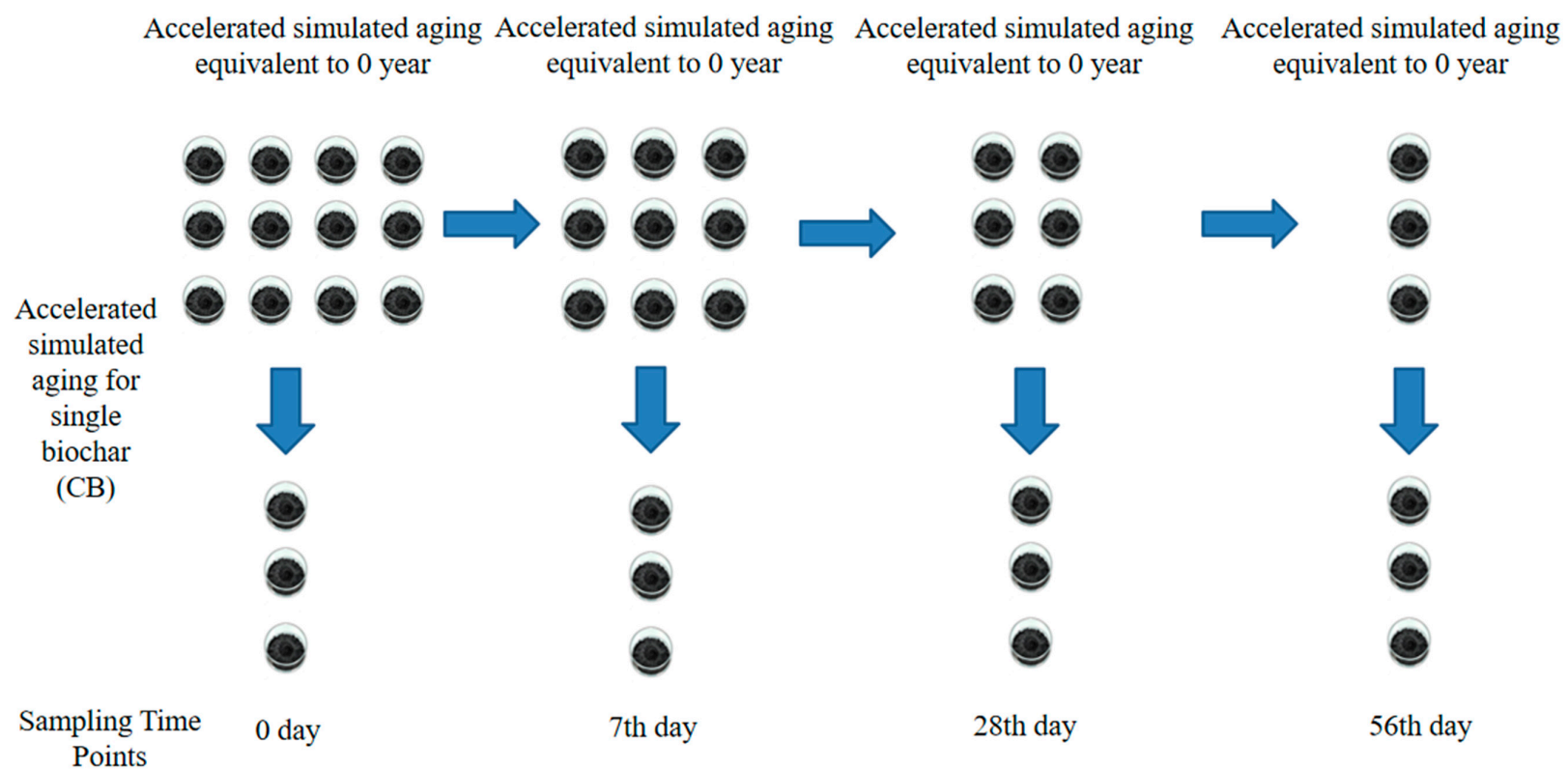


Fig. S3 The destructively sampling process for the aging of biochar amended soil (CBS)

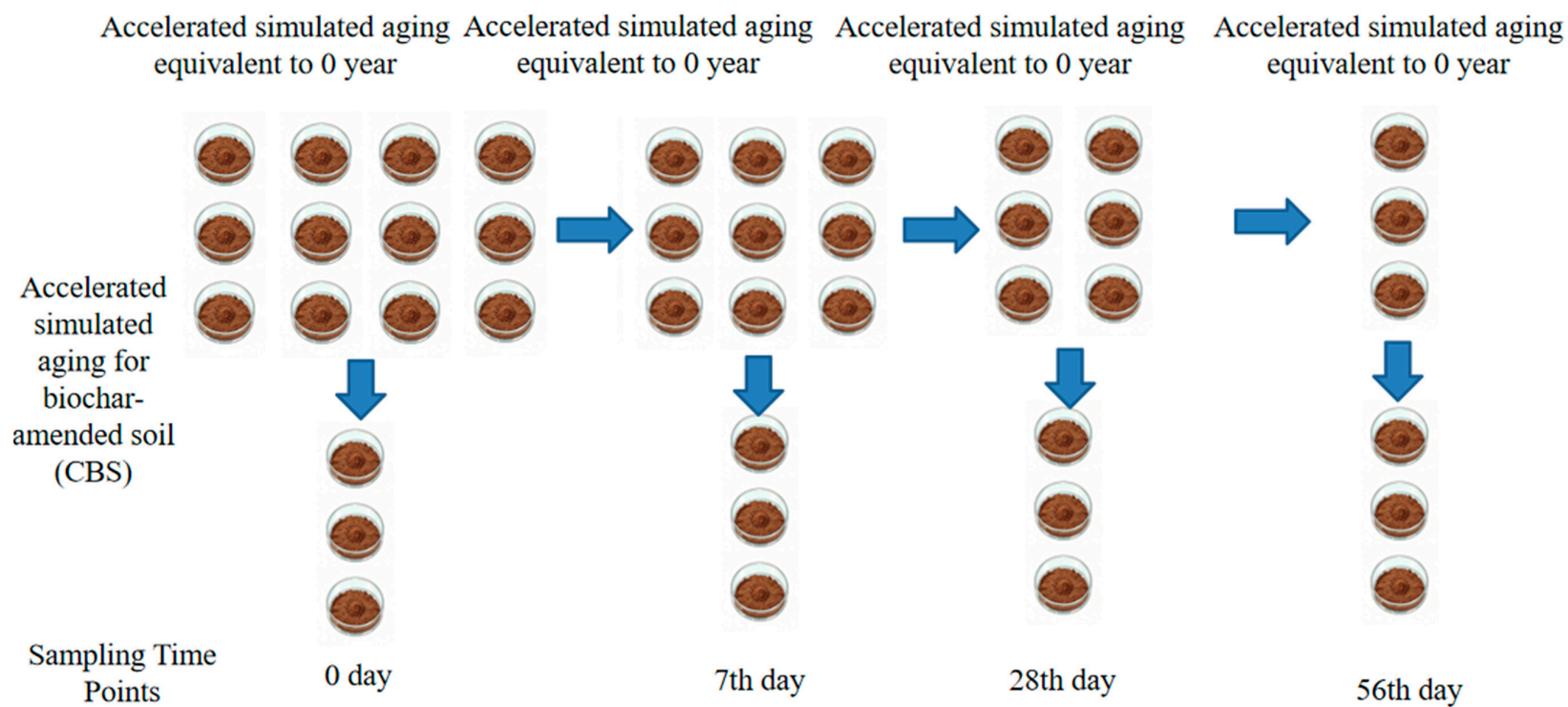


Fig. S4 N₂ adsorption-desorption isotherms of biochars before and after the accelerated simulated composite aging treatments

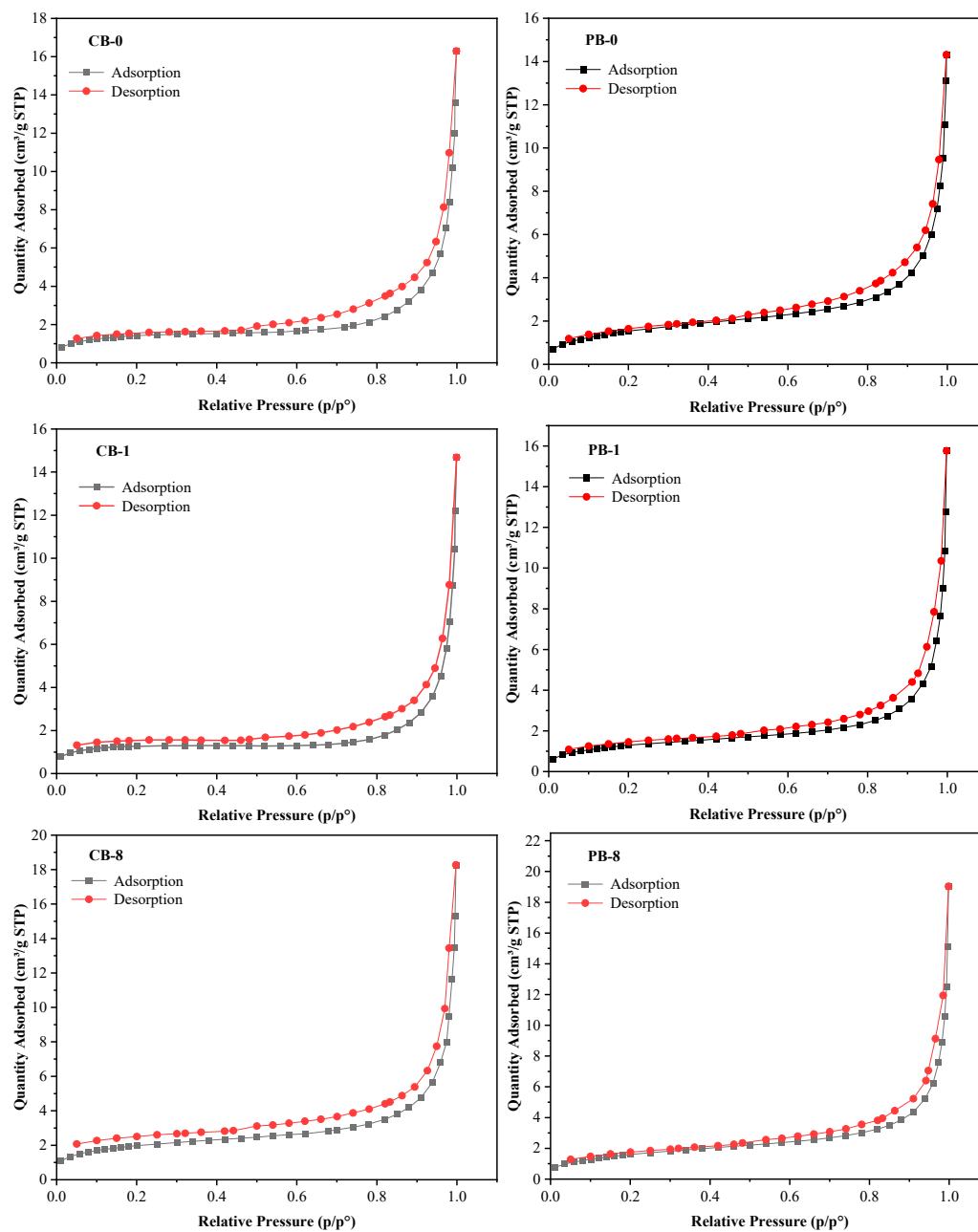


Fig. S5 The XPS full spectrum of biochar before and after the accelerated simulated composite aging

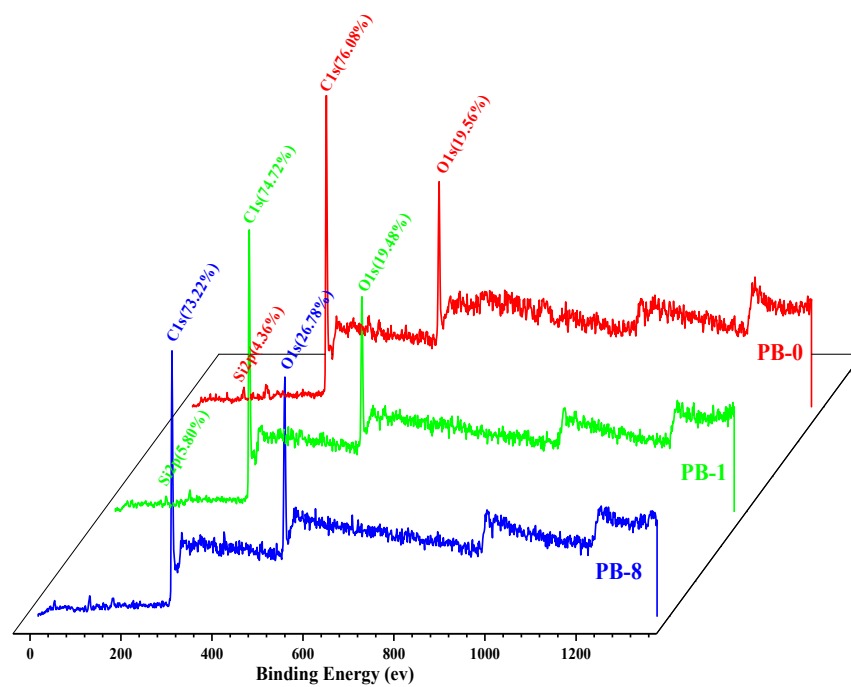
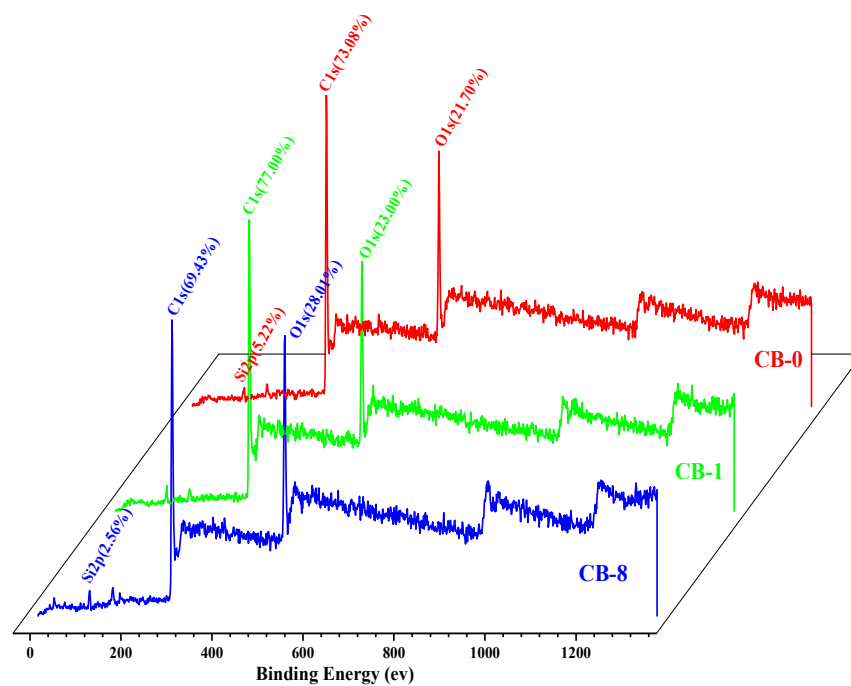


Fig. S6 C1s XPS spectra of biochars before and after the accelerated simulated composite aging

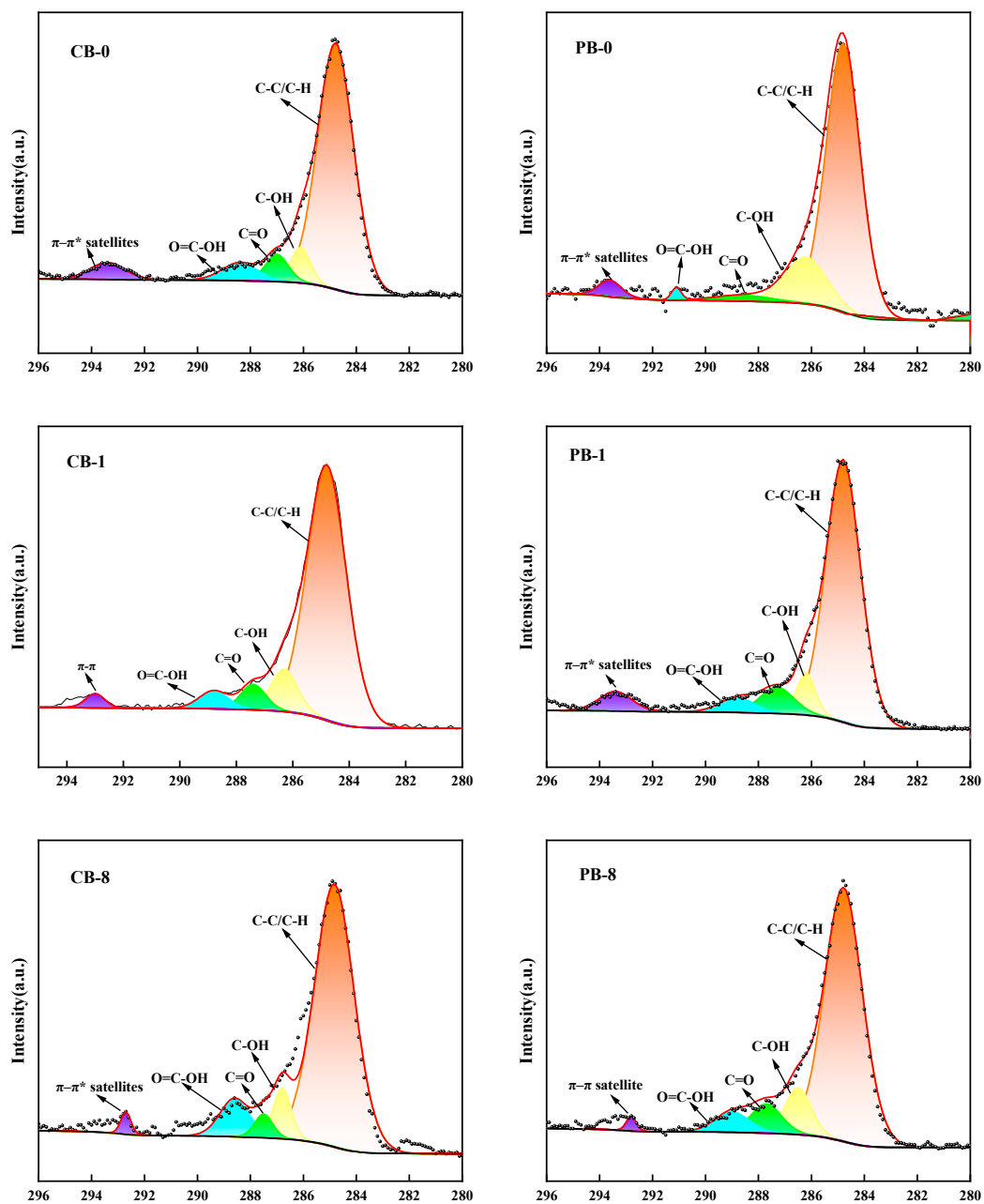
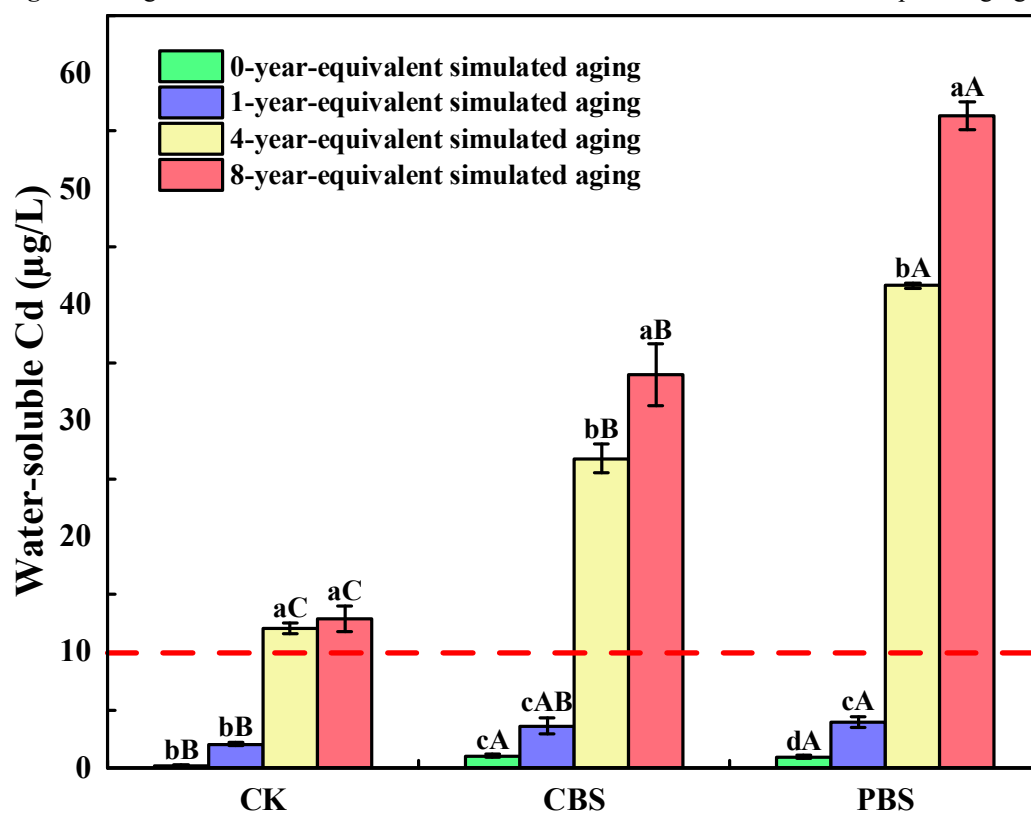


Fig. S7 Changes of soil water-soluble Cd before and after accelerated simulated composite aging



Note: Water-soluble Cd was extracted at a water-to-soil ratio of 5:1, and concentrations are expressed as $\mu\text{g}\cdot\text{L}^{-1}$. Red dashed lines indicate the Cd limits for farmland irrigation water (0.01 mg L^{-1} , GB 5084-2021)

Fig. S8 Correlation between pH and chemical fractions of Cd in soil. *, **, and *** indicate significant correlation at $p < 0.05$, $p < 0.01$, and $p < 0.001$

