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Supplementary Information

Leaching of Organic Carbon Enhances Mobility of Biochar

Nanoparticles in Saturated Porous Media

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Procedures used to determine relative hydrophobicity of biochar samples

The *n*-dodecane–water partition coefficient, K_{DW} , of biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon was assessed using a hydrocarbon partitioning test with laboratory-grade *n*-dodecane.¹ Samples were prepared by adding 4 mL of a biochar suspension to a test tube containing 1 mL of *n*-dodecane. The test tube was vortexed for 2 min, and then left undisturbed for 15 min to allow phase separation. The relative hydrophobicity was assessed as the fraction of biochar that partitioned into *n*dodecane from the aqueous phase.

The water contact angle was carried out in the air using the sessile drop method on a contact angle system OCA 20 (DataPhysics Instruments GmbH, Germany).² The contact angles reported are mean values measured for 4 μ L water droplets at five positions of each material.

Detailed procedures of column transport experiments

Transport experiments were carried out using Omnifit borosilicate cylindrical glass columns (10×0.66 cm, Bio-Chem Valve Inc., USA) packed with Lufa soil or quartz sand. Two stainless-steel screens (50-µm) were placed at both ends of the column to support the model medium and disperse the flow. Lufa soil (3.5 g) or quartz sand (3.8 g) was dry-packed into the column with gentle vibration to an average length of ~6.9 cm. The porosity and dead volume were determined with the KBr-tracer test (Fig. S1). The detailed protocols of column experiments are summarized in Table S3. The packed column was first purged with CO₂ at low pressure for 30 min to improve water saturation. Next, 100 mL DI water (3 mL/h) was injected into the column (in the upward direction) using a KDS-200 syringe pump (KD Scientific, USA), and finally, 180 mL background solution was injected into the column prior to injection of the biochar influents. (At this stage, the effluent became transparent and the absorbance of the effluent would be below 0.01, significantly lower than those of the effluents containing biochar nanoparticles (0.1-0.6). This low background absorbance was subtracted from that of the effluents of column experiments.)

The influents were prepared by diluting a stock suspension in artificial groundwater or an electrolyte solution containing Na⁺ or Ca²⁺, and then stirring for 2 h. The pH of the influents was adjusted to neutral using 0.1 mM HCl or NaOH. pH was monitored sporadically during the column experiments and was stable. The particle size distribution and ζ potential of biochar nanoparticles in the influents were measured by dynamic light scattering (DLS) and electrophoretic mobility, respectively, using a ZetaSizer Nano ZS system (Malvern Instruments, Worcestershire, U.K). The particle size distributions of biochar nanoparticles in different background solutions were given in Fig. S2. In the experiments involving a single cation, 0.68 mM was used in the experiments of Ca²⁺, consistent with the concentration of Ca²⁺ in artificial groundwater; a higher concentration (20 mM) was chosen for the experiments involving Na⁺ to render sufficient compression of double layer.

In both series of column experiments, 70 mL of each biochar influents (~20 mg/L) (equivalent to 62 or 66 pore volumes (PV) for Lufa soil and Quartz sand columns, respectively) was injected into the packed column (upward direction), followed by particle-free background solution. Column effluents were collected every 3 PV. Influent (C_0) and effluent (C) particle concentrations were determined with a UV–vis spectrophotometer (UV-2401, Shimadzu Scientific Instruments, USA) at a wavelength of 287 nm (RS300_NPs and RS300OCD_NPs), 345 nm (RS500_NPs and RS500OCD_NPs), 325 nm (MB300_NPs and MB300OCD_NPs) or 380 nm (MB500_NPs and MB500OCD_NPs), based on the predetermined calibration curves (Figs. S3 and S4). All column experiments were conducted at least in duplicate. The concentrations plotted in the breakthrough curves are the averages of the duplicates. Upon completion of the column transport experiments carried out using quartz sand, the retention profiles were determined by separating the sand into 7 segments (each of ~1 cm length) and extracting in 10 mL of DI water, by agitating for at least 3 h using

S3

oscillating shakers (KS 260 Basic, IKA) to liberate the retained biochar particles. Mass balance, 91.0 to 103%, was determined as the sum of the particle mass recovered from both the effluent and the column (Table S4). Particle remobilization experiments were carried out for selected column experiment settings (i.e., 0.68 mM CaCl₂, pH 7.0). Column flushing included four phases: 0.68 mM CaCl₂ (flushing 1); DI water (flushing 2); 20 mM NaCl (flushing 3); and DI water (flushing 4).

Calculation of attachment efficiency

To quantitatively compare the extents of particle deposition, the attachment efficiency, α , was calculated:³

$$\alpha = -\frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln(C/C_0)$$
(S1)

where d_c is the diameter of the collector grains, ε and L are the porosity and length of the packed-bed. The normalized column effluent concentration (C/C_0) in Eqn. S1 was obtained from each particle breakthrough curve by averaging the values measured between pore volumes 50 and 62 for soil columns and 53 and 66 for sand columns. The value of η_0 was calculated using the correlation developed by Tufenkji and Elimelech:³

$$\eta_{0} = 2.4 A_{\rm S}^{1/3} N_{\rm R}^{-0.081} N_{\rm Pe}^{-0.715} N_{\rm vdW}^{0.052} + 0.55 A_{\rm S} N_{\rm R}^{1.675} N_{\rm A}^{0.125} + 0.22 N_{\rm R}^{-0.24} N_{\rm G}^{1.11} N_{\rm vdW}^{0.053}$$
(S2)

where $N_{\rm R}$ is an aspect ratio, $N_{\rm Pe}$ is the Peclet number, $N_{\rm A}$ is the attraction number, $N_{\rm vdW}$ is the van der Waals number, and $N_{\rm G}$ is the gravity number (see Table S5 for detailed calculations).

Calculation of XDLVO interaction energy profiles

To qualitatively understand the transport and retention behaviors of the biochar nanoparticles prepared using pristine biochars or biochars treated to leach out organic carbon in saturated porous media (Lufa soil and quartz sand), the extended Derjaguin–Landau– Verwey–Overbeek (XDLVO) theory was used to calculate the total interaction energy as the sum of the attractive van der Waals interaction V_{VDW} (K_BT), the repulsive electrostatic double layer interaction V_{EDL} (K_BT), and the Lewis acid-base interaction V_{AB} (K_BT).^{4, 5} The equations are listed as follows:⁴⁻¹⁰

$$V_{TOT} = V_{VDW} + V_{EDL} + V_{AB}$$
(S3)

$$V_{VDW} = -\frac{Ar_{NP}}{6h\left(1 + \frac{14h}{\lambda}\right)}$$
(S4)

$$V_{EDL} = \pi r_{NP} \varepsilon_0 \varepsilon_r \left\{ 2\phi_1 \phi_2 \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\phi_1^2 + \phi_2^2) \ln \left[1 - \exp(-2\kappa h) \right] \right\}$$
(S5)

$$V_{AB} = 2\pi r_{NP} \lambda_w \Delta G_{h_0}^{AB} \exp(\frac{h_0 - h}{\lambda_w})$$
(S6)

$$A = 24\pi h_0^2 \left(\sqrt{\Upsilon_{NP}^{LW}} - \sqrt{\Upsilon_W^{LW}}\right) \left(\sqrt{\Upsilon_S^{LW}} - \sqrt{\Upsilon_W^{LW}}\right)$$
(S7)

$$\kappa = \sqrt{\frac{2N_A e^2 I}{\varepsilon_r \varepsilon_0 K_B T}}$$
(S8)

$$\Delta G_{h_0}^{AB} = 2\left[\sqrt{\gamma_w^+} \left(\sqrt{\gamma_{NP}^-} + \sqrt{\gamma_s^-} - \sqrt{\gamma_w^-}\right) + \sqrt{\gamma_w^-} \left(\sqrt{\gamma_{NP}^+} + \sqrt{\gamma_s^+} - \sqrt{\gamma_w^+}\right) - \sqrt{\gamma_{NP}^-} \sqrt{\gamma_{NP}^+} - \sqrt{\gamma_{NP}^+} \right]$$
(S9)

$$\Upsilon_i^L(1+\cos\theta) = 2\sqrt{\Upsilon_i^{LW}\Upsilon^{LW}} + 2\sqrt{\Upsilon_i^+\Upsilon^-} + 2\sqrt{\Upsilon_i^-\Upsilon^+}$$
(S10)

where *A* is the combined Hamaker constant for biochar-water-soil/sand (J), r_{NP} is the hydrodynamic radius of the aggregates under a given solution chemistry condition (m), *h* is the separation distance between nanoparticles and collectors (m), a characteristic wavelength (λ) of 100 nm was assumed in the calculation,¹¹ ε_0 is the vacuum permittivity (8.85×10⁻¹² C²/Jm), ε_r is the relative dielectric permittivity of water (78.4), ϕ_1 and ϕ_2 are the surface potentials of biochar nanoparticles (Table 2) and soil/sand grains (Table S6), respectively, κ (m⁻¹) is the Debye reciprocal length and the values are 2.02×10⁸, 4.65×10⁸, and 1.49×10⁸ in

AGW, 20 mM NaCl, and 0.68 mM CaCl₂, respectively, λ_w is the characteristic decay length of acid–base interactions in water (1.0 nm at 20 °C), $\Delta G_{h_0}^{AB}$ represents the acid–base interaction free energy per unit area corresponding to h_0 (mJ/m²), h_0 is the value for the minimum equilibrium distance between nanoparticles and soil/sand surface and equals to 0.157 nm,¹² γ_{NP}^{LW} , γ_{W}^{LW} and γ_{S}^{LW} are the Lifshitz–van der Waals interfacial tension values for nanoparticles, water and soil/sand, respectively, N_A is the Avogadro number (6.02×10²³ mol⁻¹), e is the electron charge (-1.60×10⁻¹⁹ C), I is the ionic strength of the background electrolyte, K_B is Boltzmann constant (1.38×10⁻²³ J/K), and T is Kelvin temperature (298 K). For biochar nanoparticles, the values of γ_{NP}^{LW} , γ_{NP}^{+} , γ_{NP}^{-} were calculated using equation S10. The previously reported interfacial tension values of water ($\gamma_w^L = 72.8$, $\gamma_w^{LW} = 21.8$, and $\gamma_w^+ =$ $\gamma_w^- = 25.5$ mJ/ m²), glycerol ($\gamma_g^L = 64.0$, $\gamma_g^{LW} = 34.0$, $\gamma_g^+ = 3.92$, and $\gamma_g^- = 57.4$ mJ/m²), and diiodomethane ($\gamma_d^L = 50.8$, $\gamma_d^{LW} = 50.8$, $\gamma_d^+ = \gamma_d^- = 0$ mJ/m²) were used.¹⁰ The detailed parameters and results of equations S7, S9 and S10 are summarized in Table S7.

Properties	Quartz sand, 50-70 mesh particle size (Sigma-Aldrich)	Lufa soil		
Grain size d ₅₀ (µm)	255	295		
Particle size distribution	sand [99%]	sand [86.0%] clay [2.5%] silt [11.5%]		
Classification	а	loamy sand		
Organic matter (%)	а	0.71		
pH-value (0.01 M CaCl ₂)	6.7 ± 0.3	4.9 ± 0.3		
Cation exchange capacity (meq/100g)	а	4.2 ± 0.6		
uniformity	а	0.46		

Table S1. Physicochemical properties of the porous media (Quartz sand and Lufa soil) used in the transport experiments.

^{*a*} not applicable or not measured.

Ions	Concentration (mM)
HCO ₃ -	0.43
SO_4^{2-}	0.39
NO ₃ -	0.62
Cl-	0.64
Ca ²⁺	0.68
Mg^{2+}	0.24
Na ⁺	0.43
K^+	0.20

 Table S2. Recipe of artificial groundwater.

Column	Porous	Biochar nanoparticles ^b	Background solution	Ionic strength	Length	Bulk density	Porosity ^b	Pore-water	Biochar conc. (ma/L)
1	I ufa soil	RS300 NPs	AGW nH 7.5	3.78	<u>(CIII)</u>	<u>(g/clll²)</u> 1 44	0.45	10	<u>(IIIg/L)</u> 19.0
1 1#	Luía soil	$\frac{RS300}{NPs}$	AGW, pH 7.5	3.78	6.9	1.44	0.45	10	20.2
1 7	Lufa soil	RS300CD NPs	AGW, pH 7.5	3.78	6.9	1.44	0.45	10	20.2
2 2#	Lufa soil	RS300OCD_NPs	AGW, pH 7.5	3.78	7.0	1.44	0.45	10	20.0
3	Lufa soil	$\frac{RS500 \text{ CD}_{141} \text{ s}}{RS500 \text{ NPs}}$	AGW nH 7.5	3.78	6.9	1.42	0.40	10	20.0
3#	Lufa soil	RS500 NPs	AGW nH 7.5	3 78	6.9	1.44	0.45	10	19.2
4	Lufa soil	RS500OCD NPs	AGW nH 7.5	3 78	6.9	1.44	0.45	10	19.2
4#	Lufa soil	RS5000CD_NPs	AGW nH 7.5	3 78	6.8	1.11	0.45	10	19.9
5	Lufa soil	MB300 NPs	AGW nH 7.5	3 78	6.9	1.17	0.45	10	20.0
5#	Lufa soil	MB300 NPs	AGW pH 7.5	3 78	6.9	1 44	0.45	10	21.4
6	Lufa soil	MB3000CD NPs	AGW pH 7.5	3 78	6.9	1 44	0.45	10	18.9
6#	Lufa soil	MB300OCD NPs	AGW, pH 7.5	3.78	7.0	1.42	0.46	10	20.5
7	Lufa soil	MB500 NPs	AGW. pH 7.5	3.78	6.9	1.44	0.45	10	19.9
7#	Lufa soil	MB500 NPs	AGW. pH 7.5	3.78	6.9	1.44	0.45	10	20.7
8	Lufa soil	MB500OCD NPs	AGW. pH 7.5	3.78	6.9	1.44	0.45	10	19.6
8#	Lufa soil	MB500OCD NPs	AGW, pH 7.5	3.78	6.8	1.47	0.45	10	21.4
9	Quartz sand	RS300 NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	19.8
9#	Quartz sand	RS300 NPs	AGW, pH 7.5	3.78	7.0	1.53	0.42	10	19.8
10	Quartz sand	RS300OCD NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	19.5
10#	Quartz sand	RS300OCD NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.9
11	Quartz sand	RS500_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	19.6
11#	Quartz sand	RS500_NPs	AGW, pH 7.5	3.78	6.8	1.57	0.41	10	22.0
12	Quartz sand	RS500OCD_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.2
12#	Quartz sand	RS500OCD_NPs	AGW, pH 7.5	3.78	6.8	1.57	0.41	10	20.8
13	Quartz sand	MB300_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.4
13#	Quartz sand	MB300_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.4
14	Quartz sand	MB300OCD_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.2
14#	Quartz sand	MB300OCD_NPs	AGW, pH 7.5	3.78	7.0	1.53	0.42	10	21.2
15	Quartz sand	MB500_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	20.1
15#	Quartz sand	MB500_NPs	AGW, pH 7.5	3.78	7.0	1.53	0.42	10	20.1
16	Quartz sand	MB500OCD_NPs	AGW, pH 7.5	3.78	6.9	1.55	0.42	10	19.7

 Table S3. Protocols of column experiments.

16#	Quartz sand	MB500OCD_NPs	AGW, pH 7.5	3.78	6.8	1.57	0.41	10	20.9
17	Lufa soil	RS300_NPs	20 mM NaCl, pH 7.0	20	6.9	1.44	0.45	10	19.0
17#	Lufa soil	RS300_NPs	20 mM NaCl, pH 7.0	20	7.0	1.42	0.46	10	22.0
18	Lufa soil	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	6.9	1.44	0.45	10	19.2
18#	Lufa soil	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	6.9	1.44	0.45	10	20.2
19	Quartz sand	RS300_NPs	20 mM NaCl, pH 7.0	20	6.9	1.55	0.42	10	19.3
19#	Quartz sand	RS300_NPs	20 mM NaCl, pH 7.0	20	6.8	1.57	0.41	10	19.3
20	Quartz sand	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	6.9	1.55	0.42	10	19.2
20#	Quartz sand	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	6.9	1.55	0.42	10	19.8
21	Lufa soil	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.44	0.45	10	21.0
21#	Lufa soil	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.44	0.45	10	21.0
22	Lufa soil	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.44	0.45	10	20.2
22#	Lufa soil	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	7.0	1.42	0.46	10	20.8
23	Quartz sand	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.55	0.42	10	21.8
23#	Quartz sand	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.55	0.42	10	20.6
24	Quartz sand	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.55	0.42	10	20.4
24#	Quartz sand	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.8	1.57	0.41	10	21.0
25	Lufa soil	RS500_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.45	0.45	10	18.5
25#	Lufa soil	RS500_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.8	1.47	0.45	10	21.5
26	Lufa soil	RS500OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.45	0.45	10	19.3
26#	Lufa soil	RS500OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	6.9	1.45	0.45	10	21.3

^{*a*} All column experiments were conducted in duplicate. The symbol # indicates that the column is the respective replicate of the column indicated by the numerical number. ^{*b*} The acronyms RS and MB stand for rice straw and moso bamboo, respectively, the biochar feed stocks; the numbers 300 and 500 indicate pyrolysis temperature; the biochars receiving treatment to leach out the organic carbon are indicated with the suffix "OCD", which stands for organic-carbon-deficient.

	•			-							•				
С	Porosity	=	(column	volume	—	mass	of	soil	or	sand/density	of	soil	or	sand)/column	volume.

Column no ^{<i>a</i>} .	Porous medium	Biochar nanoparticles ^b	Background solution	Ionic strength (mM)	Effluent mass ^c (%)	Recovered mass d (%)	Mass balance ^e (%)
9	Quartz sand	RS300_NPs	AGW, pH 7.5	3.78	49.2	41.8	91.0
10	Quartz sand	RS300OCD_NPs	AGW, pH 7.5	3.78	53.6	39.9	93.5
11	Quartz sand	RS500_NPs	AGW, pH 7.5	3.78	14.2	79.2	93.4
12	Quartz sand	RS500OCD_NPs	AGW, pH 7.5	3.78	16.1	80.2	96.3
13	Quartz sand	MB300_NPs	AGW, pH 7.5	3.78	22.4	70.2	92.6
14	Quartz sand	MB300 OCD_NPs	AGW, pH 7.5	3.78	25.9	72.3	98.2
15	Quartz sand	MB500_NPs	AGW, pH 7.5	3.78	16.1	79.0	95.1
16	Quartz sand	MB5000CD_NPs	AGW, pH 7.5	3.78	18.1	80.3	98.4
19	Quartz sand	RS300_NPs	20 mM NaCl, pH 7.0	20	71.2	29.9	101
20	Quartz sand	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	72.0	28.0	100
23	Quartz sand	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	59.5	43.7	103
24	Quartz sand	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	61.7	35.1	96.8

Table S4. Mass balance of column experiments carried out using quartz sand.

^{*a*} All column experiments were conducted in duplicate. For each column experiment presented, average measurement from two separate experiments are shown.

^{*b*} The acronyms RS and MB stand for rice straw and moso bamboo, respectively, the biochar feed stocks; the numbers 300 and 500 indicate pyrolysis temperature; the biochars receiving treatment to leach out the organic carbon are indicated with the suffix "OCD", which stands for organic-carbon-deficient.

^c Effluent mass was the percentage of biochar nanoparticles passed through columns.

^d Recovered mass was the percentage of biochar nanoparticles recovered from columns.

^e Mass balance was calculated as: effluent mass + recovered mass.

Table S5. Su	mmary of dimensionless	parameters governing particle filtration.
Parameter	Definition ^a	Physical interpretation

	2	
arameter	Definition ^{<i>a</i>}	Physical interpretation
N_{R}	$N_R = \frac{d_p}{d_c}$	aspect ratio
N_{Pe}	$N_{Pe} = \frac{Ud_{\rm c}}{D_{\infty}}$	Peclet number characterizing ratio of convective transport to diffusive transport
$N_{\rm A}$	$N_{\rm A} = \frac{A}{12\pi\mu a_{\rm p}^2 U}$	attraction number representing combined influence of van der Waals attraction forces and fluid velocity on particle deposition rate due to interception
$N_{ m vdW}$	$N_{\rm vdW} = \frac{A}{kT}$	van der Waals number characterizing ratio of van der Waals interaction energy to the particle's thermal energy
$N_{ m G}$	$N_{\rm G} = \frac{2}{9} \frac{a_{\rm p}^2 (\rho_{\rm p} - \rho_{\rm f})g}{\mu U}$	gravity number; ratio of Stokes particle settling velocity to approach velocity of the fluid
C1		1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -

^{*a*} The parameters in the various dimensionless groups are as follows: d_p is the particle diameter, d_c is the collector diameter, U is the fluid approach velocity, D_{∞} is the bulk diffusion coefficient (described by Stokes-Einstein equation), A is the Hamaker constant, k is the Boltzmann constant, T is fluid absolute temperature, a_p is particle radius, ρ_p is the particle density, ρ_f is the fluid density, μ is the absolute fluid viscosity, and g is the gravitational acceleration.

Solution chemistry	Lufa soil	Quartz sand
AGW, pH 7.5	-16.8 ± 1.5	-17.9 ± 1.8
20 mM NaCl, pH 7.0	-50.6 ± 3.0	-47.4 ± 2.4
0.68 mM CaCl ₂ , pH 7.0	-20.5 ± 1.6	-21.2 ± 2.0

Table S6. Surface potential of the porous media (Lufa soil and quartz sand) used in the transport experiments under different solution chemistry conditions.

Properties		Lufa soil	Quartz sand ^{<i>a</i>}	RS300_NPs	RS300OCD_NPs	RS500_NPs	RS500OCD_NPs	MB300_NPs	MB300OCD_NPs	MB500_NPs	MB500OCD_NPs
	water	25.6	7.00	86.3	91.4	111	113	108	112	123	124
contact angle (°C)	glycerol/ formamide	53.7	40.9	77.1	83.5	104	105	109	107	102	102
	diiodomethane	34.6	7.00	56.5	58.4	62.1	64.4	48.1	53.7	71.1	73.3
surface	$\gamma^{\rm LW}$	42.2	39.2	30.6	29.5	27.4	26.0	35.3	32.2	22.3	22.1
tension components	γ^+	0.15	1.40	0.11	2.2×10^{-5}	1.16	0.95	4.41	2.61	$2.2 imes 10^{-4}$	$8.6 imes 10^{-6}$
(mJ m ⁻²)	γ^{-}	53.4	47.8	4.99	4.02	1.54	1.55	7.09	5.76	1.20	1.26
	-						Lufa soil columr	1			
combined Hamaker constant (4) (10 ⁻²¹ I)				2.93	2.59	1.91	1.48	4.33	3.41	0.17	0.13
$\Delta G_{h_0}^{AB}$ (mJ m ⁻²)	_			-4.93	-5.60	-17.6	-17.1	-8.94	-9.20	-14.1	-13.8
	-						Quartz sand colun	nn			
combined Hamaker constant $(A) (10^{-21} \text{ J})$				2.55	2.25	1.66	1.29	3.77	2.97	0.15	0.11
$\Delta G_{h_0}^{AB}$ (mJ m ⁻²)				-4.17	-4.73	-14.6	-14.2	-7.47	-7.69	-11.8	-11.5

Table S7. Contact angle values, surface tension components, combined Hamaker constant (*A*), and $\Delta G_{h_0}^{AB}$ used in the calculation of XDLVO interaction energy profiles.

^{*a*} From Morrow et al. (2005).¹³

The acronyms RS and MB stand for rice straw and moso bamboo, respectively, the biochar feed stocks; the numbers 300 and 500 indicate pyrolysis temperature; the biochars receiving "OCD", which to leach out the organic carbon are indicated with the suffix stands for organic-carbon-deficient. treatment

				Ionic	Φ	max	đ	$\Phi_{ m sec}$	
Column	Porous	Biochar	De alemana de alection	strength	height	distance	depth	distance	
no.	medium	nanoparticles a	Background solution	(mM)	$(K_{\rm B}T)$	(nm)	$(K_{\rm B}T)$	(nm)	
1	Lufa soil	RS300_NPs	AGW, pH 7.5	3.78	59.4	5.2	-0.07	50	
2	Lufa soil	RS300OCD_NPs	AGW, pH 7.5	3.78	58.5	5.4	-0.06	50	
3	Lufa soil	RS500_NPs	AGW, pH 7.5	3.78	21.2	7.0	-0.04	50	
4	Lufa soil	RS500OCD_NPs	AGW, pH 7.5	3.78	28.0	7.0	-0.03	50	
5	Lufa soil	MB300_NPs	AGW, pH 7.5	3.78	41.8	6.0	-0.10	45	
6	Lufa soil	MB300OCD_NPs	AGW, pH 7.5	3.78	41.8	6.0	-0.09	45	
7	Lufa soil	MB500_NPs	AGW, pH 7.5	3.78	26.3	7.0	-0.002	65	
8	Lufa soil	MB500OCD_NPs	AGW, pH 7.5	3.78	27.2	7.0	-0.002	65	
9	Quartz sand	RS300_NPs	AGW, pH 7.5	3.78	65.4	5.0	-0.06	50	
10	Quartz sand	RS300OCD_NPs	AGW, pH 7.5	3.78	65.2	5.2	-0.05	50	
11	Quartz sand	RS500_NPs	AGW, pH 7.5	3.78	29.2	7.0	-0.03	50	
12	Quartz sand	RS500OCD_NPs	AGW, pH 7.5	3.78	30.4	7.0	-0.02	50	
13	Quartz sand	MB300_NPs	AGW, pH 7.5	3.78	47.3	5.8	-0.09	45	
14	Quartz sand	MB300OCD_NPs	AGW, pH 7.5	3.78	48.9	5.8	-0.07	45	
15	Quartz sand	MB500_NPs	AGW, pH 7.5	3.78	30.1	6.5	-0.002	65	
16	Quartz sand	MB500OCD_NPs	AGW, pH 7.5	3.78	31.0	6.5	-0.001	65	
17	Lufa soil	RS300_NPs	20 mM NaCl, pH 7.0	20	165	2.9	-0.27	22	
18	Lufa soil	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	142	3.1	-0.23	22	
19	Quartz sand	RS300_NPs	20 mM NaCl, pH 7.0	20	167	2.7	-0.23	22	
20	Quartz sand	RS300OCD_NPs	20 mM NaCl, pH 7.0	20	145	3.0	-0.20	22	
21	Lufa soil	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	106	5.2	-0.03	75	
22	Lufa soil	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	108	5.2	-0.03	75	
23	Quartz sand	RS300_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	114	4.8	-0.03	75	
24	Quartz sand	RS300OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	114	5.0	-0.02	75	
25	Lufa soil	RS500_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	54.8	7.0	-0.02	75	
26	Lufa soil	RS500OCD_NPs	0.68 mM CaCl ₂ , pH 7.0	2.04	55.4	7.0	-0.01	75	

Table S8. Calculated maximum energy barriers (Φ_{max}), secondary energy minimum depth (Φ_{sec}), and the respective separation distances of particle–collector extended DLVO interaction energy profiles.

^{*a*} The acronyms RS and MB stand for rice straw and moso bamboo, respectively, the biochar feed stocks; the numbers 300 and 500 indicate pyrolysis temperature; the biochars receiving treatment to leach out the organic carbon are indicated with the suffix "OCD", which stands for organic-carbon-deficient.



Fig. S1. Representative breakthrough curve of conservative tracer (Br⁻) in (a) Lufa soil and (b) quartz sand. The line was plotted by fitting the breakthrough data with the one-dimensional steady-state advection–dispersion equation.



Fig. S2. Intensity-weighted particle size distribution of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon under different solution chemistry conditions: (a) AGW, pH 7.5; (b) 20 mM NaCl, pH 7.0; (c) 0.68 mM CaCl₂, pH 7.0. The acronyms RS and MB stand for rice straw and moso bamboo, respectively, the biochar feed stocks; the numbers 300 and 500 indicate pyrolysis temperature; the biochars receiving treatment to leach out the organic carbon are indicated with the suffix "OCD", which stands for organic-carbon-deficient.



Fig. S3. UV/Vis spectra of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon dispersed in DI water (20 mg/L).



Fig. S4. Calibration curves as absorbance at the wavelength of 287, 345, 325 or 380 nm versus concentration of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon.



Fig. S5. Particle size distribution and representative transmission electron microscopy (TEM) images of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon. Particle size was determined from 5 different TEM images over 100 particles. No significant differences in particle size between biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon were observed, based on Tukey's HSD test at p < 0.05.



Fig. S6. Atomic force microscopy (AFM) images (a1-h1) of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon. Diameter (lateral size, x-axis) and thickness (height profile, y-axis) from AFM analysis (a2-h2) of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon on the dotted line in panel (a1-h1). No significant differences in particle average vertical and lateral size between biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic pristine biochars and biochars treated to leach out organic carbon on the dotted line in panel (a1-h1). No significant differences in particle average vertical and lateral size between biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon were observed, based on Tukey's HSD test at p < 0.05.



Fig. S7. X-ray photoelectron spectroscopy (XPS) spectra of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon. The peaks with the binding energy of ~284.6, ~286.1, ~287.2, and ~289.0 eV are assigned to the carbon atoms in aromatic rings (C-C/C=C), epoxy/hydroxyl (C-O-C/C-OH), carbonyl (C=O) and carboxyl (O-C=O), respectively.



Fig. S8. Fourier transform infrared (FTIR) spectra of the biochar nanoparticles prepared using pristine biochars and biochars treated to leach out organic carbon.



Fig. S9. Amounts of organic carbon (OC) released from rice-straw- and moso-bambooderived biochars produced at two different temperatures (300 and 500 °C). Error bars represent \pm one standard deviations of duplicates.



Fig. S10. Three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectra of the organic carbon (OC) released from rice-straw- and moso-bamboo-derived biochars produced at two different temperatures (300 and 500 °C), showing that the amounts of organic carbon (OC) released from biochars were highly dependent on pyrolysis temperature and feed stock.¹⁴ For both RS- and MB-derived biochars, the intensity of the fluorescent peak at the excitation–emission wavelengths (Ex/Em) of <250/380–480 nm (corresponding to humic-acid-like organics¹⁵) was much weaker in OC released from high-temperature biochars than that from low-temperature biochars, indicating that the amounts of OC released from biochars declined significantly with increasing of pyrolysis temperature. The intensity of the fluorescent peak (<250/380–480 nm) was also much weaker in OC released from MB-derived biochars than that from RS-derived biochars (mainly low-temperature biochars), suggesting that herbace-derived biochars (in this case the RS biochars) released higher OC amounts than wood-derived biochars (MB biochars). Similar results were observed previously.^{14, 16}







Fig. S12. Extended DLVO biochar–soil interaction energy profiles in artificial groundwater. The insets show the close-up of the respective secondary energy minimum region.



Fig. S13. Selected scanning electron microscopy (SEM) images (a and b) and associated energy-dispersive X-ray spectra (EDX) (c and d) of biochar nanoparticles deposited on Lufa soil and quartz sand (AGW, pH 7.5). Red circles indicate deposited particles. The points marked with "+" in (a) and (b) were selected for EDX analysis.



Fig. S14. Extended DLVO biochar–sand interaction energy profiles in artificial groundwater. The insets show the close-up of the respective secondary energy minimum region.

Fig. S15. Retention profiles of biochar nanoparticles in quartz sand saturated with artificial groundwater. Error bars represent variations of duplicate column tests (detailed column setups are summarized in Table S3).

Fig. S16. Extended DLVO biochar–soil interaction energy profiles in 0.68 mM CaCl₂ at pH 7.0. The insets show the close-up of the respective secondary energy minimum region.

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