Supplementary Material for

Long-term Sorption of Lincomycin to Biochars: The Intertwined Roles of Pore Diffusion and Dissolved Organic Carbon

Cheng-Hua Liu[a, b], Ya-Hui Chuang[a, c], Hui Li[a], Stephen A. Boyd[a], Brian J. Teppen[a], Javier M. Gonzalez[d], Cliff T. Johnston[e], Johannes Lehmann[f], and Wei Zhang[a, b, *]

[a] Department of Plant, Soil and Microbial Sciences, Michigan State University, East Lansing, Michigan 48824, United States

[b] Environmental Science and Policy Program, Michigan State University, East Lansing, Michigan 48824, United States

[c] Department of Soil and Environmental Sciences, National Chung-Hsing University, Taichung 402, Taiwan

[d] National Soil Erosion Research Lab, Agricultural Research Service, United States Department of Agriculture, West Lafayette, IN 47907, United States

[e] Department of Agronomy, Purdue University, West Lafayette, IN 47907, United States

[f] Soil and Crop Sciences Section, School of Integrative Plant Science, Cornell University, Ithaca, NY 14853, United States

*Corresponding author: Dr. Wei Zhang, Address: 1066 Bogue ST RM A516, East Lansing, MI 48824, United States; Tel: 517-353-0471; Fax: 517-355-0270; Email: weizhang@msu.edu

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Content

28 pages, 13 figures, and 6 tables

S1. Supplemental Materials and Methods

Sorbent characterization. Surface area and porosity of biochars were determined by CO_2 adsorption isotherms at 273 K in the relative pressure (P/P_0) range of 0.004 to 0.032. Specific surface area (SSA) and micropore volume (V_{mic}) were then calculated based on the Langmuir equation and the Dubinin-Astakhov equation, respectively. Prior to CO_2 adsorption, all biochars were degassed at 300 °C for 12 hours under N_2 so that the vapor emission from biochars was sufficiently low to perform the measurement. It was noted that the used degassing temperature and duration could potentially increase the surface area and pore volume of biochars due to the removal of poorly-carbonized fraction during degassing (Sigmund et al., 2017) because biochar surface and pores originally clogged by volatiles become more accessible. As a result, the actual surface area and porosity of biochars may be overestimated. Measuring the change of surface area and porosity of biochars due to the release of dissolved organic carbon (DOC) is important to studying the underlying sorption mechanisms. To limit the loss of DOC during degassing, relatively lower degassing temperature and longer degassing duration were used in our preliminary test. However, the preliminary determination of surface area and porosity by N_2 adsorption at 77 K for BM300 (a poorly-carbonized biochar sample) was not successful following degassing at 150 °C for 48 hours under vacuum, which was attributed to the interference from a continuous emission of volatile organic compounds from the leachable DOC and poorly-carbonized organic fractions in biochars during measurement. Since we were not able to successfully measure surface area and porosity of biochars without removing volatiles by degassing, the determination of detailed pore size distribution before and after the DOC release was not performed in this study.

Biochar Suspensions. To generate a biochar suspension for the zeta potential measurements, 8 mg each biochar was mixed with 8 mL 0.02 M background electrolyte (6.7 mM NaCl, 2.5 mM Na_2CO_3, 2.5 mM $NaHCO_3$, and 200 mg L^{-1} NaN_3.) in amber glass vials and then shaken end-over-end for 1 day. Afterwards, the vials were allowed standing for 30 min and then the top 1 mL of the suspension was withdrawn and measured for the zeta potential by the Zetasizer Nano-ZS. The remained suspensions were used to determine solution pH of the suspension (10.0 ± 0.1 for all tested biochars).

To measure the biochar colloid size after the DOC release, biochars were suspended in 0.01M NaCl or 0.01M NaOH solution (1:1 solid/water ratio) and shaken end-over-end for 1 day. After shaking, the vials were allowed standing for 30 min and then the top 1 mL of the biochar suspension was withdrawn and measured for particle size by the Zetasizer Nano-ZS.

Determination of Lincomycin Concentrations. The concentration of lincomycin in solutions were determined by a Shimadzu Prominence high-performance liquid chromatograph coupled to an Applied Biosystems Sciex 3200 triple quadrupole mass spectrometer (LC-MS/MS) (Chuang et al., 2015). The analytical column was an Agilent ZORBAX Eclipse Plus C18 column (Agilent Technologies, Santa Clara, CA, USA) with 50 mm length × 2.1 mm diameter and 5 μm particle size. The mobile phase A consisted of DI water and 0.3% formic acid. The mobile phase B consisted of 1:1 (v/v) acetonitrile-methanol mixture and 0.3% formic acid. Data were acquired using a gradient condition of 0–40% B in 0–1 min, 40–70% B in 1–2 min, 70–80% B in 2–3 min, 80–100% B in 3–3.5 min, and 100% B for 0.5 min. The flow rate was set to 0.35 mL min^{-1} and the injection volume was set to10 μL. The electrospray ionization (ESI) in positive ion mode was used in the tandem quadrupole MS. Lincomycin was detected and quantified using a multiple

reaction monitoring mode with a precursor/product transition of 407.2/126.2. The retention time was 2.37 min and the instrument detection limit of lincomycin was 0.2 pg.

Determination of DOC Concentration. The concentration of DOC released from the biochars were determined by our recently developed UV absorption method with a Varian Cary 50 Bio UV-visible spectrophotometer (Liu et al., 2019). We considered the biochar DOC was a mixture of the acid-soluble (AS) and acid-precipitable (AP) fractions and the fraction of AS can be calculated via:

$$f_{\mathrm{AS}} = \frac{1.135e-2.813}{e-1.797} \qquad (1)$$

where f_{AS} is the proportion of the AS fraction ($0 \leq f_{\mathrm{AS}} \leq 1$), and e is the E_2/E_3 ratio. The E_2/E_3 ratio was calculated as the ratio of decadic absorption coefficient (a, cm^{-1}) at 254 nm (a_{254}) to 365 nm (a_{365}), where the a was calculated by UV-vis absorbance (unitless) divided by path length (cm). If calculated f_{AS} value is < 0 or > 1, it will be assumed to be 0 or 1, respectively. Then, the biochar DOC concentration in solution (in the unit of mg-C L^{-1}) can be calculated via:

$$\mathrm{DOC} = \frac{\alpha_{254}}{0.0232f_{\mathrm{As}}+0.0642(1-f_{\mathrm{As}})} \qquad (2)$$

The DOC determined by the UV absorption method was generally in good agreement with the DOC measured by a total organic carbon (TOC) analyzer. The instrument detection limit of UV-visible spectrophotometer was 0.0037 cm^{-1} at 254 nm and 0.0030 cm^{-1} at 365 nm.

Effect of Biochar-DOC as Co-solute on Lincomycin Sorption. To extract the DOC from the biochars, 500 mg of each selected biochar were mixed with 50 mL of DI water in 50 mL polypropylene (PP) centrifuge tubes, and then shaken end-over-end at 30 rpm in dark for 7 days. Afterwards the tubes were centrifuged at 8,000 × g for 20 min, and the supernatants were then vacuum-filtered through a 0.45-μm membrane (mixed cellulose esters). The final filtrates were collected as the DOC stock solutions, and the DOC concentrations were determined by a

Shimadzu TOC-V_{CPN} TOC analyzer (Shimadzu, Japan). Aliquots of each DOC stock solutions were further diluted 10-fold with a lincomycin solution (lincomycin concentration of 1111 μg L^{-1} and ionic strength of 0.022 M background electrolytes) to achieve the initial lincomycin concentration of 1000 μg L^{-1}, ionic strength of 0.02 M, and DOC concentration of 17.2, 7.94, 11.1, and 10.9 mg-C L^{-1} for BM300-, DM300-, PM300-, and DDM500-DOC, respectively. For comparison, a lincomycin solution without DOC was prepared using the same protocol but replacing the DOC stock solution with DI water. The prepared lincomycin solutions with and without DOC were denoted as lincomycin/DOC and lincomycin/DI, respectively. Thereafter, the lincomycin sorption kinetics in the presence of DOC were carried out using WW500 biochar, which was selected because of its low DOC content. Briefly, 8 mL of each lincomycin/DOC and lincomycin/DI solutions were mixed with 8 mg WW500 biochar in vials, and then the vials were shaken end-over-end at 30 rpm in dark for the duration of 1 day to 60 days. The other procedures were same as described in the sorption kinetics section. In addition, the control experiments of lincomycin/DOC solutions without WW500 biochars were also performed using the same protocol.

Lincomycin Sorption to Washed Biochars. To wash out the DOC, 500 mg of each selected biochar (BM300, BM600, DM300, PM300, and DDM500) were mixed with 50 mL of 0.1 M NaOH (only for BM300, BM600, and DM300) or DI water in vials and then end-over-end shaken at 30 rpm in dark for 1 day or 40 days, respectively. The suspensions were then centrifuged at 8,000 × *g* for 20 min, and the supernatant was collected. The supernatant was vacuum-filtered through a 0.45-μm membrane and determined for the DOC concentration by the TOC analyzer after appropriate sample dilution. The treated biochar pellets were re-dispersed with 50 mL DI water and re-centrifuged for five times to remove remaining salt and DOC, and

then freeze-dried to obtain the DOC-washed biochars. The sorption kinetics of lincomycin on the washed biochars were conducted as previously describe. Briefly, 8 mg of each washed biochar were suspended in 8 mL of 1000 μg L^{-1} lincomycin solution, and then end-over-end shaken at 30 rpm in dark for the duration of 1 to 30 days. The rest sampling and analysis procedures were identical as previously described.

Lincomycin Binding to Biochar-DOC in Solution. Briefly, 7.2 mL of each DI-water-extracted DOC solution as described above (40-d extraction) was mixed with 0.8 mL of lincomycin solution (lincomycin concentration of 10,000 μg L^{-1} and ionic strength of 0.2 M background electrolytes) in vials to acquire the lincomycin/DOC mixture solution with the initial lincomycin concentration of 1000 μg L^{-1}, ionic strength of 0.02 M, and DOC concentration of 186, 93.8, 97.4, and 89.6 mg-C L^{-1} for BM300-, DM300-, PM300-, and DDM500-DOC, respectively. The vials were then end-over-end shaken at 30 rpm in dark for 1 day. Afterwards, the lincomycin/DOC mixture solution was passed through an Oasis hydrophilic–lipophilic balance (HLB) cartridge (Waters, Milford, MA, USA), which was preconditioned with 3.0 mL of methanol and 3.0 mL of DI water. At this step, the DOC-bound lincomycin in solution could pass through the HLB cartridge and the freely dissolved lincomycin in solution would be retained by the HLB cartridge. The retained freely-dissolved lincomycin was further eluted from the HLB cartridge with 5.0 mL of methanol, and then determined the concentration by LC-MS/MS. Finally, the DOC-bound lincomycin concentration was calculated by the difference between initial applied lincomycin concentration and freely dissolved lincomycin concentration in solutions.

Extraction of Sorbed Lincomycin. Following the sorption kinetics after 240 days (when over 70% of tested biochars were approaching the apparent sorption equilibrium), two vials of

each biochar in the kinetic sorption experimental set were retrieved. The suspensions in vials were stirred with a PTFE-coated micro stir bar, and 2 mL of each suspension was uniformly withdrawn, filtered, and determined for the lincomycin concentration in filtrates by the LC-MS/MS. In addition, another 1 mL of each suspension was placed into a vial containing 4 mL of acetonitrile/methanol (8/2 in v/v) extraction solvent. The vials were end-over-end shaken at 30 rpm in dark for 7 days and then sonicated in ultrasonic bath (Model FS110H, Fisher Scientific, Pittsburgh, PA, USA) for 60 min at 50 °C. The suspensions were then centrifuged, filtered, and determined for the lincomycin concentration by the LC-MS/MS as described previously. The extraction recovery of lincomycin from biochars were calculated by mass balance.

To examine the effect of sorption equilibration time on the extraction recovery of sorbed lincomycin on the biochars, 8 mg of DM600 biochar sample were added into 8 mL of lincomycin solution with an initial concentration of 500 μg L^{-1}, initial pH of 10, and ionic strength of 0.02 M. The suspensions were end-over-end shaken at 30 rpm in dark for 1, 4, and 30 days. The other sorption/extraction procedures were identical as described earlier, except for a shorter extraction time of 1 day.

S2. Supplemental Results and Discussion

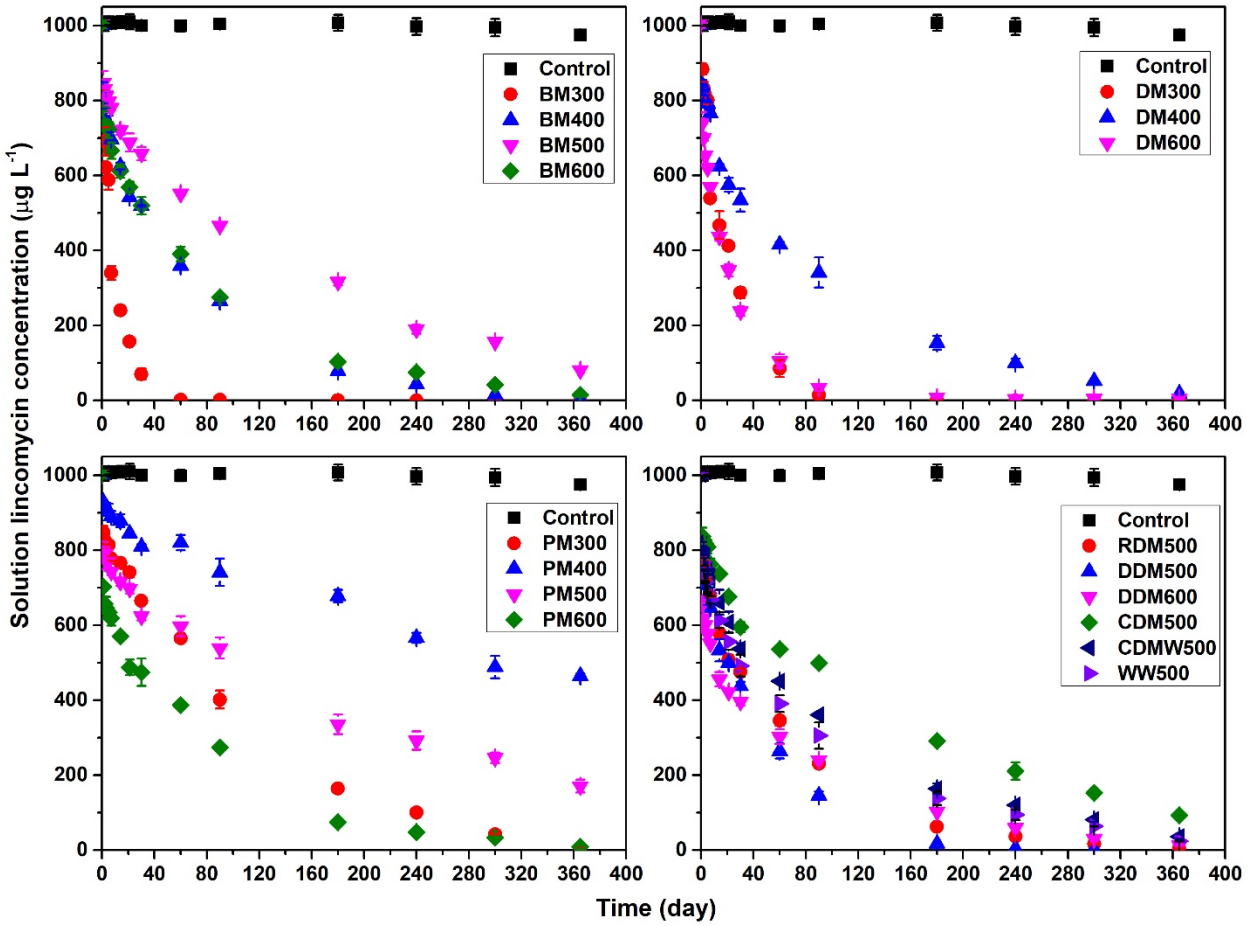


Figure S1. Lincomycin concentrations in solution over time in the kinetic sorption experiments for the 17 tested biochars. Control was the biochar-free lincomycin solution.

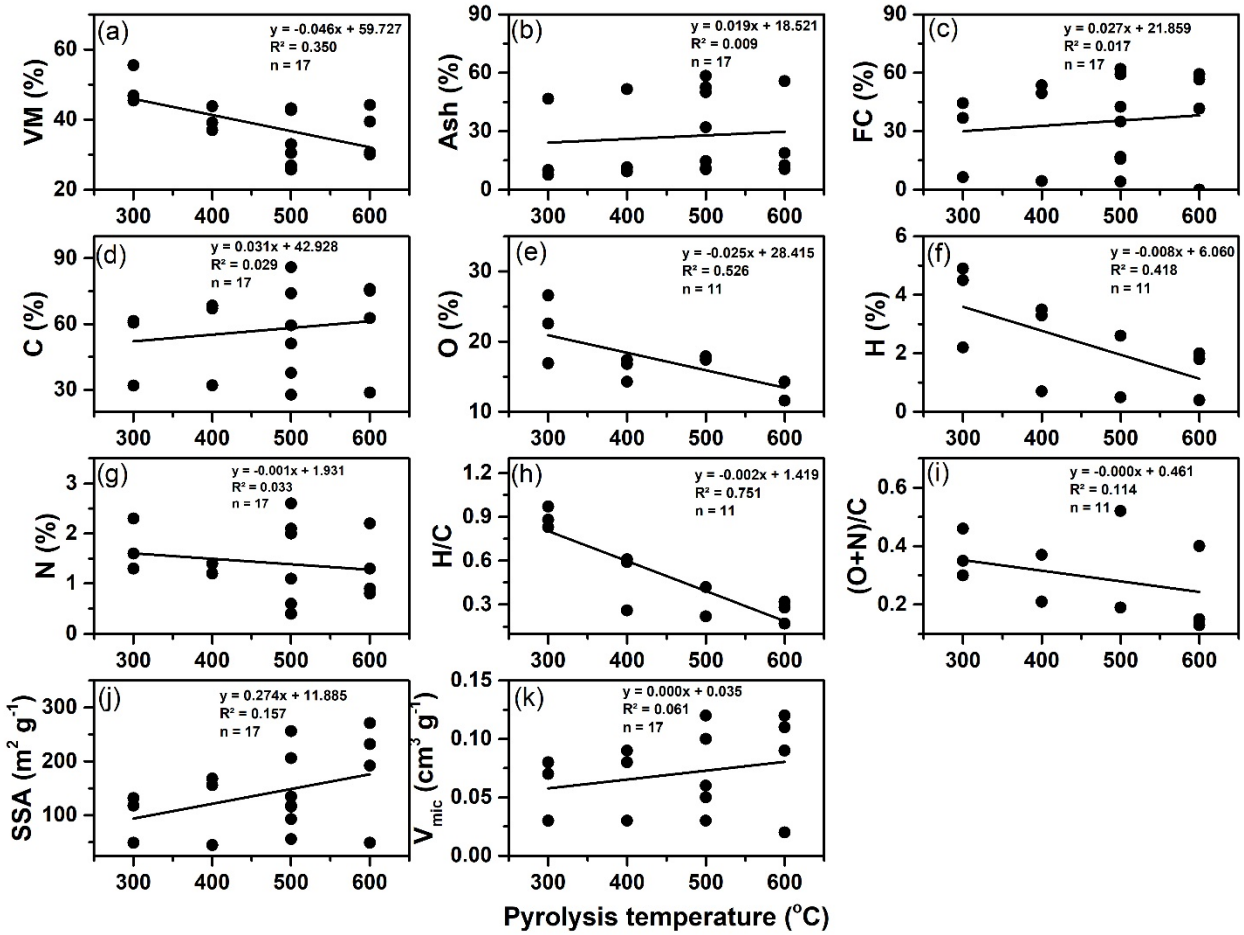


Figure S2. Relationship of (a) volatile matter (VM) content, (b) Ash content, (c) fixed carbon (FC) content , (d) total C content, (e) total O content, (f) total H content, (g) total N content, (h) H/C atomic ratio, (i) (O+N)/C atomic ratio, (j) specific surface area (SSA), and (k) micropore volume (V_{mic}) versus pyrolysis temperature of biochars.

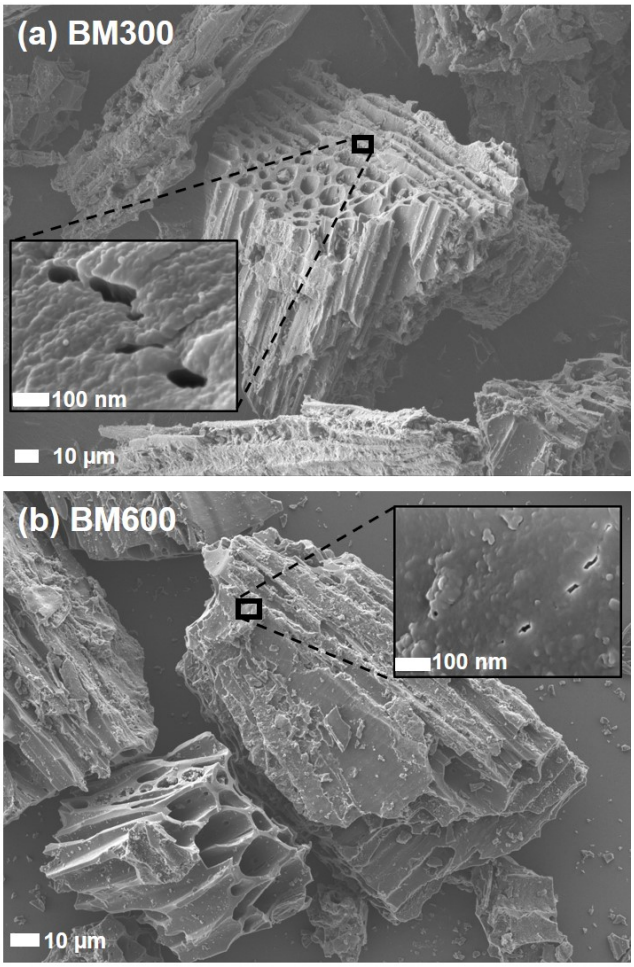


Figure S3. Scanning electron microscopy images of raw biochars: (a) BM300 (bull manure biochar produced at 300 °C) and (b) BM600 (bull manure biochar produced at 600 °C).

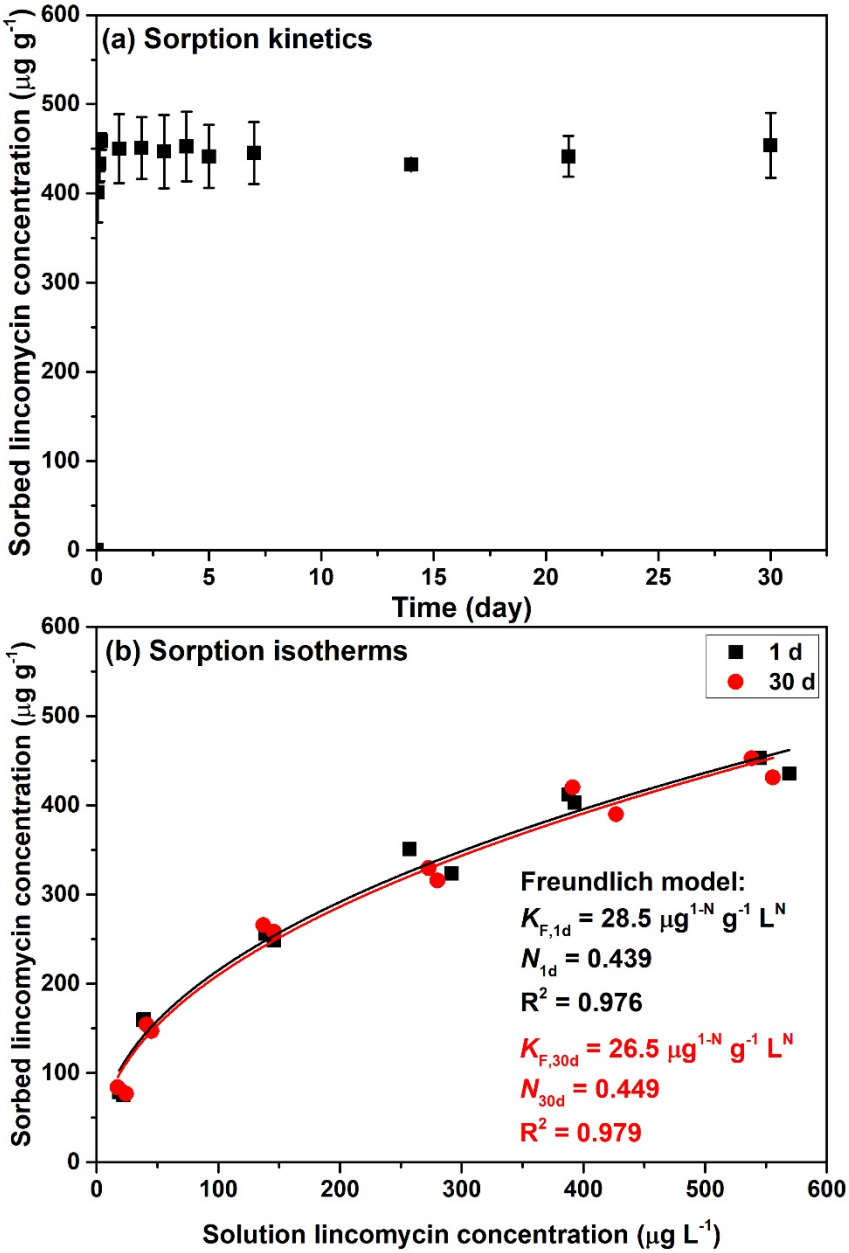


Figure S4. Sorption kinetics (a) and isotherms (b) of lincomycin to graphite. The solid lines were fitted by the Freundlich model. The K_d values were 28.5 L g^{-1} (1-d sorption equilibration time) and 26.5 L g^{-1} (30-d sorption equilibration time) at C_w = 1 μg L^{-1}.

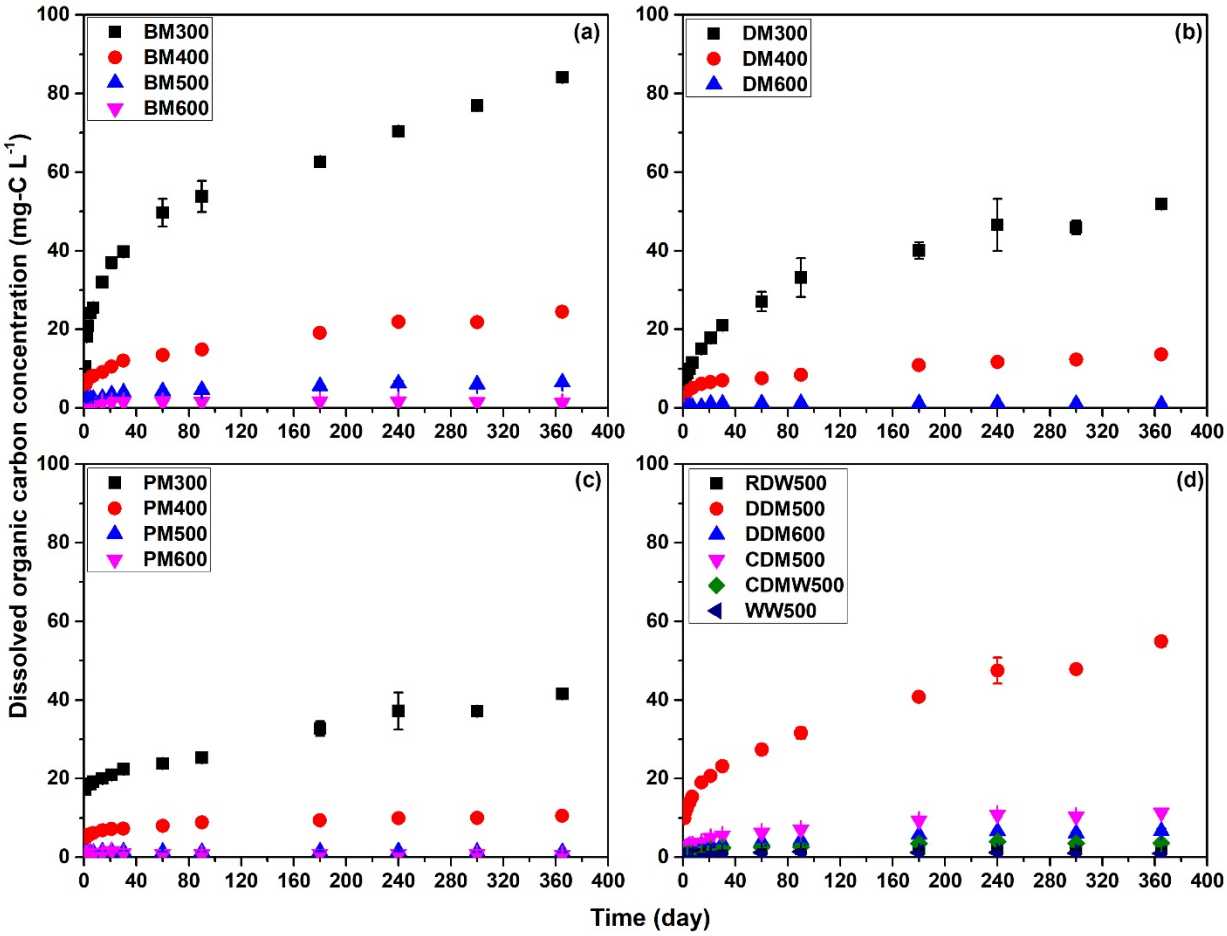


Figure S5. Long-term release of dissolved organic carbon from biochars.

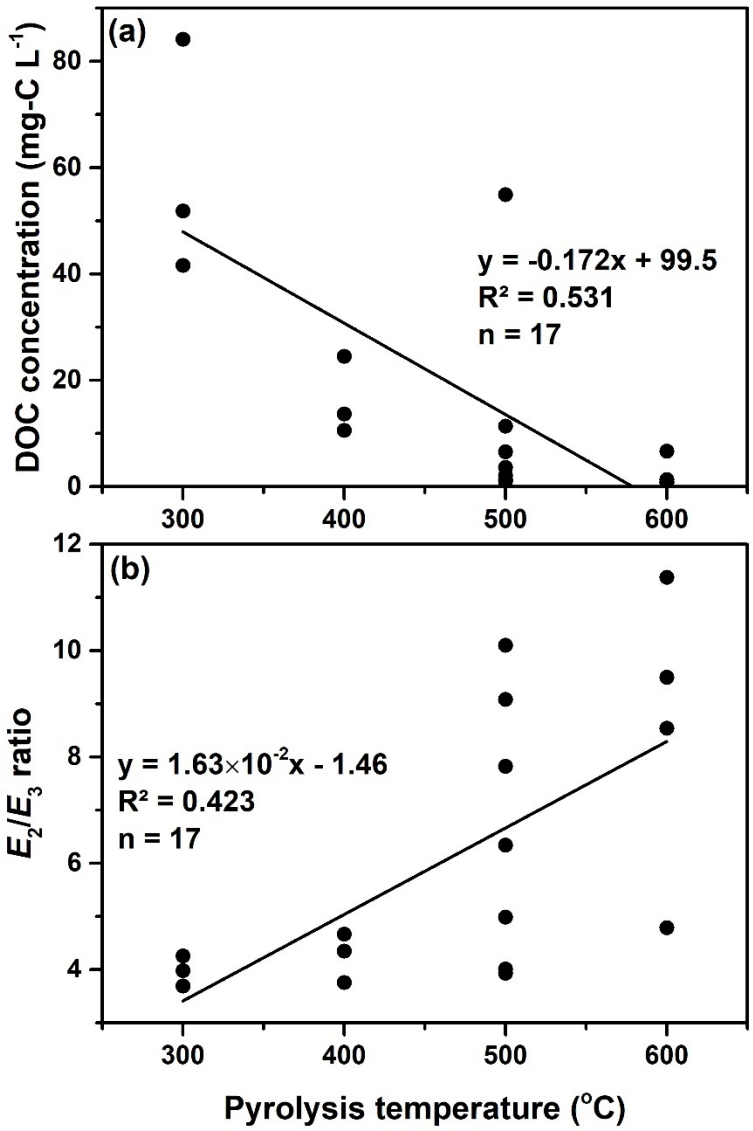


Figure S6. The relationship of concentration (a) and E_2/E_3 ratio (b) of biochar-DOC versus pyrolysis temperature. The tested biochar-DOC samples were collected from long-term sorption kinetics at 365 days.

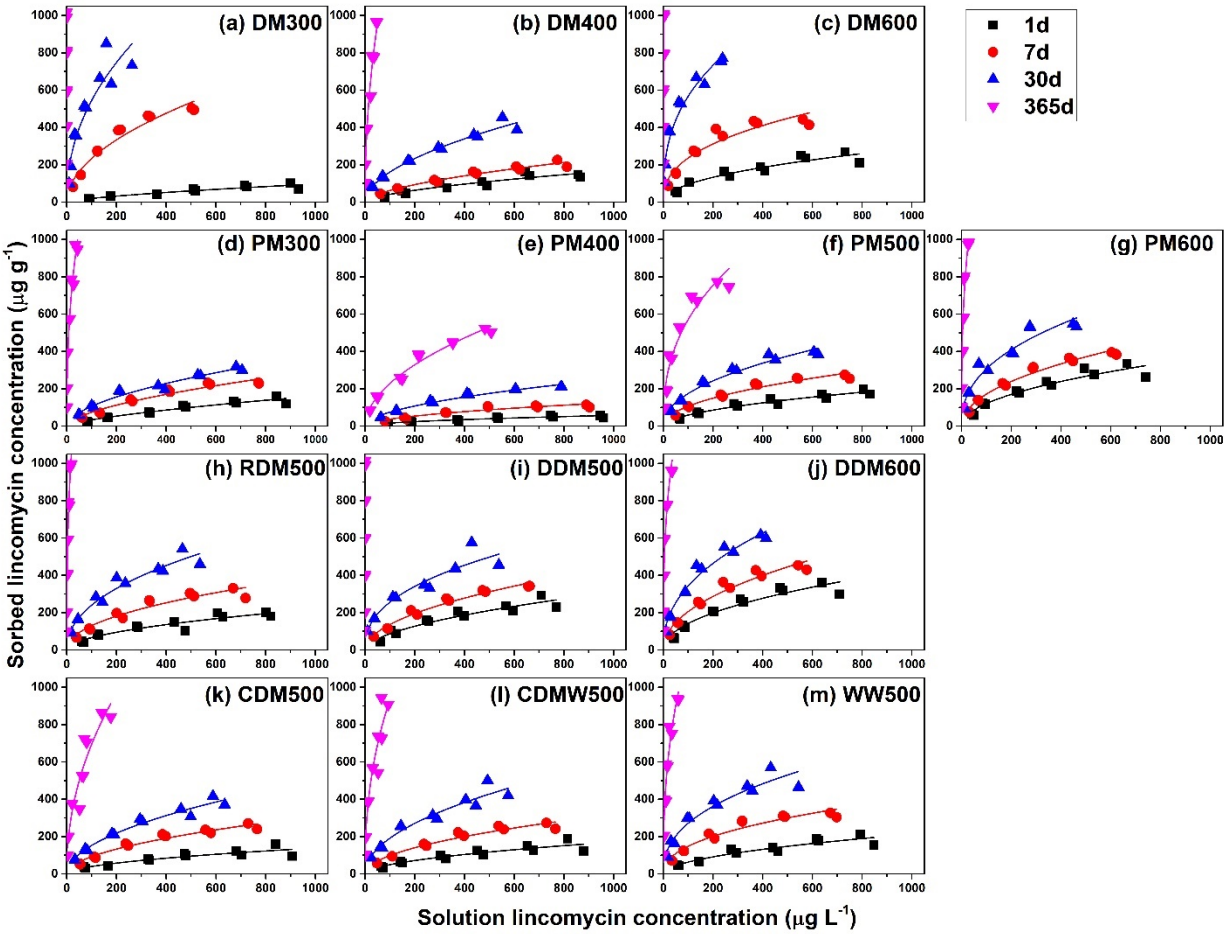


Figure S7. Quasi-equilibrium sorption isotherms of lincomycin to biochars at 1, 7, 30, and 365 days: (a) DM300, (b) DM400, (c) DM600, (d) PM300, (e) PM400, (f) PM500, (g) PM600, (h) RDM500, (i) DDM500, (j) DDM600, (k) CDM500, (l) CDMW500, and (m) WW500. The solid lines were fitted with the Freundlich isotherm model.

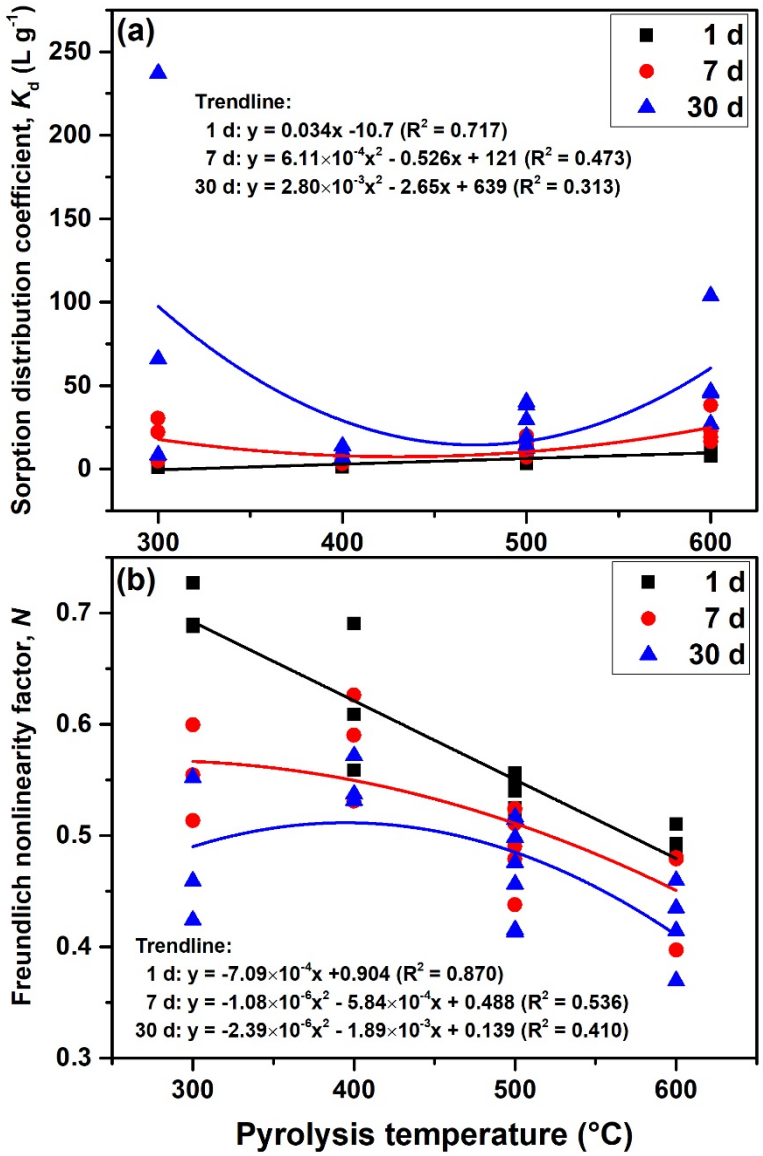


Figure S8. The relationship of sorption distribution coefficient (K_d) and Freundlich nonlinearity factor (N) versus pyrolysis temperature for biochars.

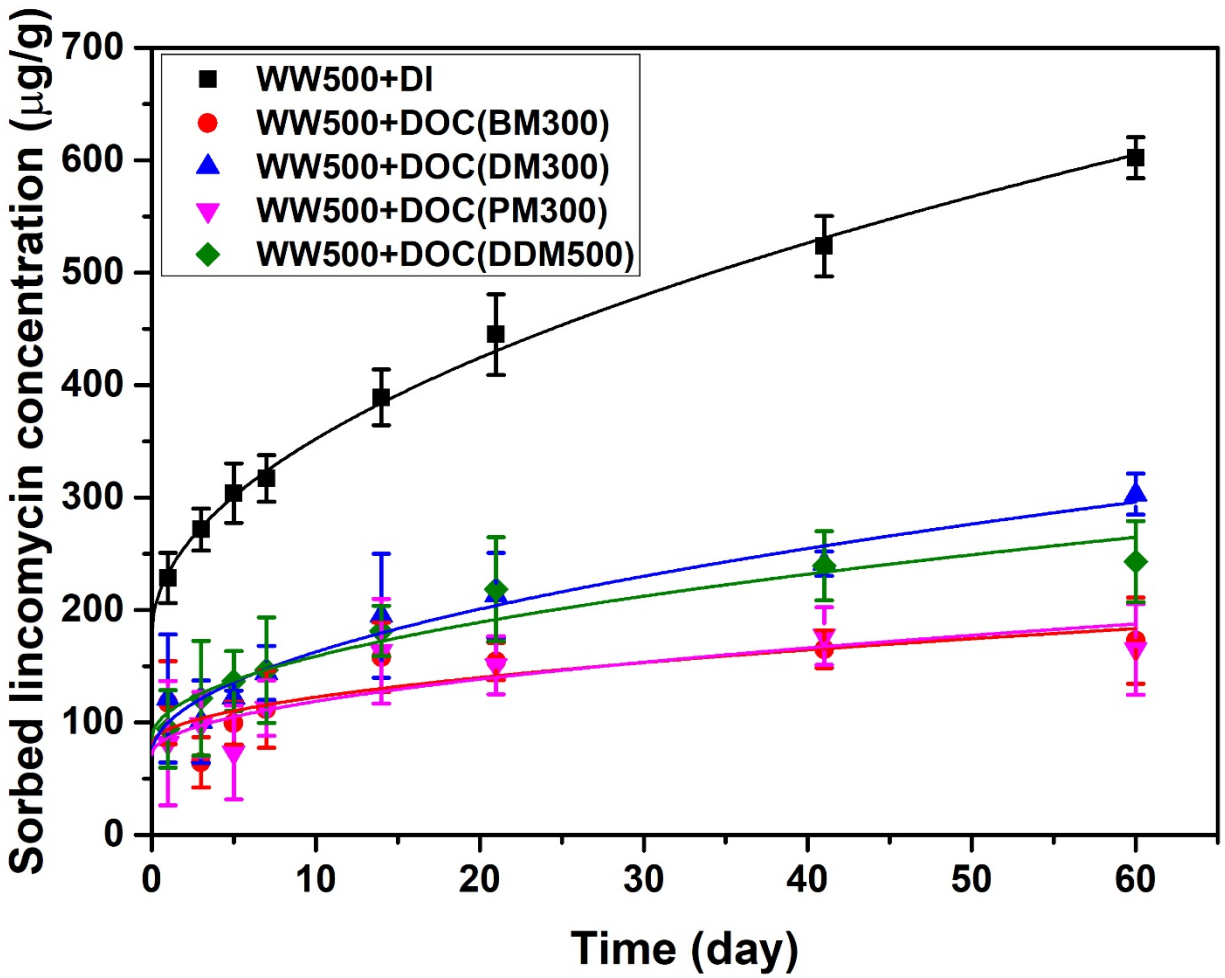


Figure S9. The effect of biochar-derived DOC as co-solutes on sorption kinetics of lincomycin by WW500 biochar (WW500+DI was the control of absence DOC). The sorption data were fitted by the intraparticle diffusion model (solid line). The symbols and error bars represent mean and standard deviation of duplicates.

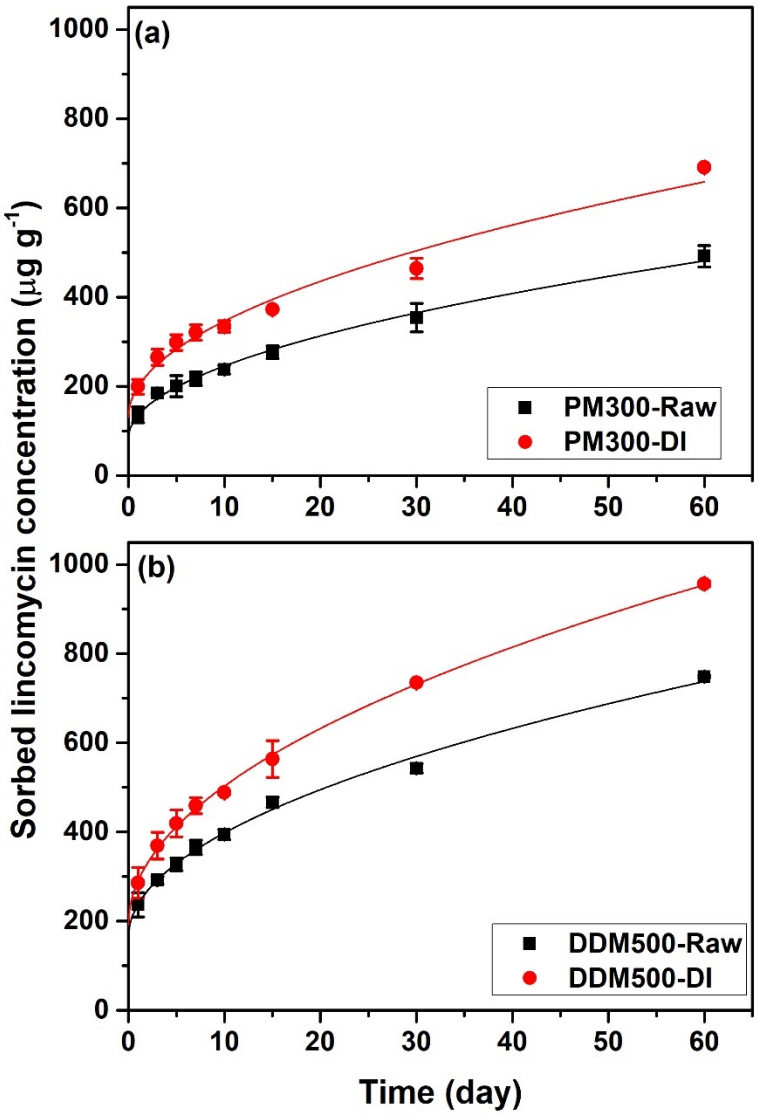


Figure S10. Long-term kinetics of lincomycin sorption by raw- and DI-water-washed biochars: (a) PM300 and (b) DDM500. The sorption data were fitted by the intraparticle diffusion model (solid line). The symbols and error bars represent mean and standard deviation of duplicates.

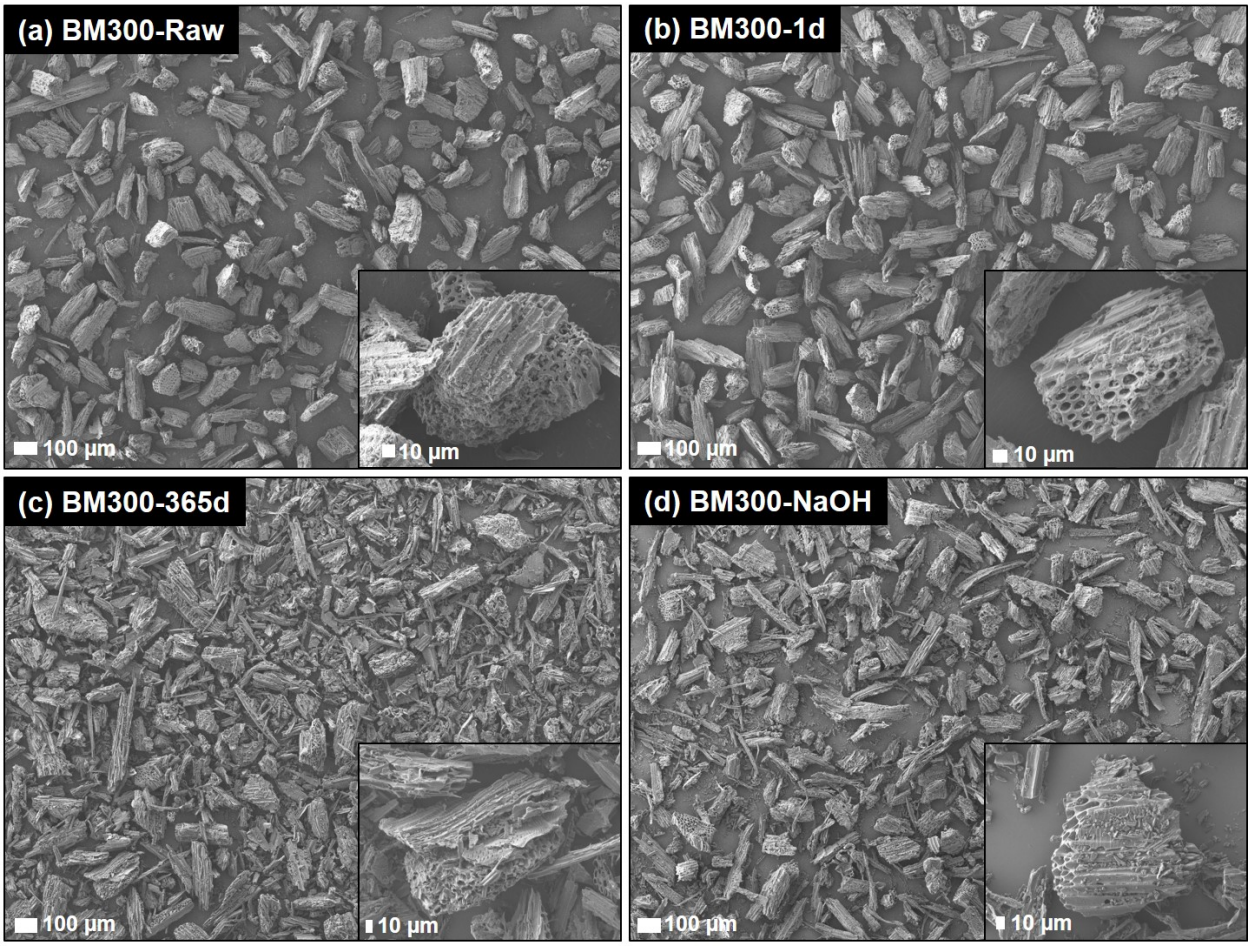


Figure S11. Scanning electron microscopy images of bull manure biochar pyrolyzed at 300°C (BM300): (a) raw BM300 without treatment, (b) BM300 after 1-d background solution exposure, (c) BM300 after 365-d background solution exposure, and (d) BM300 after 1-d 0.1 M NaOH solution exposure. Background solution contained 1000 µg L^{-1} lincomycin, 6.7 mM NaCl, 2.5 mM Na_2CO_3, 2.5 mM $NaHCO_3$, and 200 mg L^{-1} NaN_3.

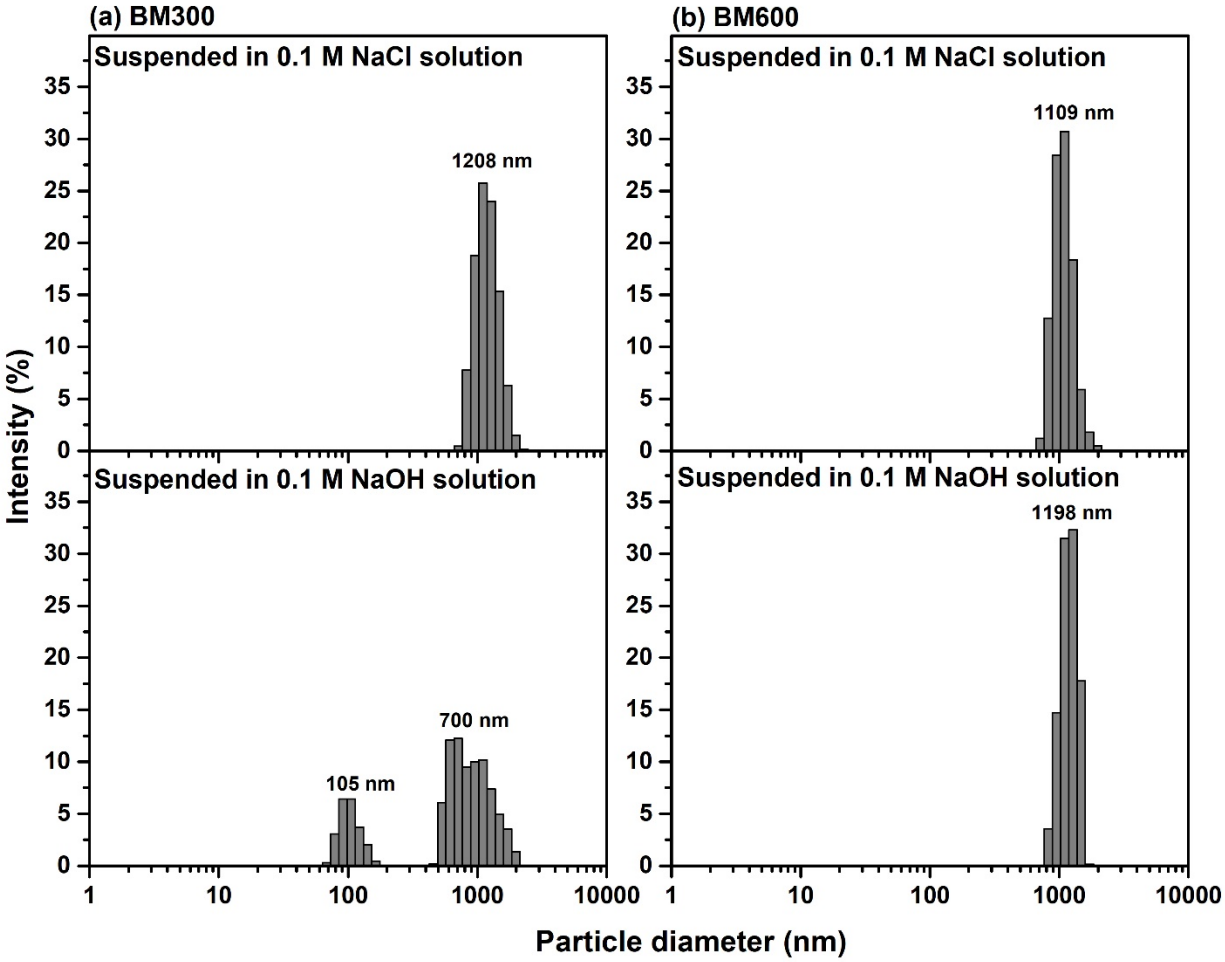


Figure S12. Particles size distribution of (a) bull manure biochar pyrolyzed at 300°C (BM300) and (b) bull manure biochar pyrolyzed at 600°C (BM600) suspended in 0.1 M NaCl (upper panel) or in 0.1 M NaOH (lower panel) after one-day exposure.

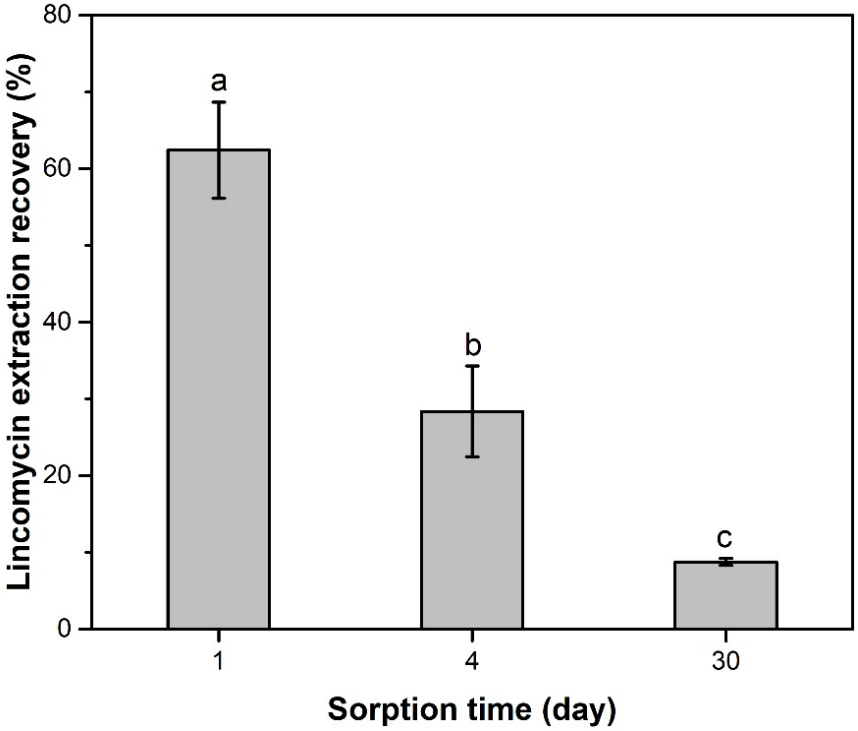
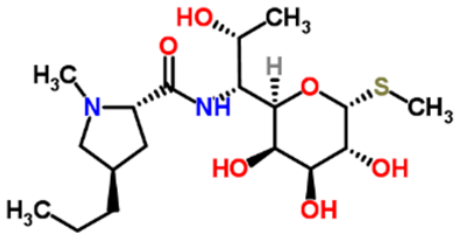


Figure S13. The effect of sorption time on lincomycin extraction recovery of DM600 biochar. Means with different small letters are significantly different (n = 2, $p < 0.05$, one-way ANOVA with post-hoc Tukey test).

Table S1. Physicochemical properties of lincomycin.

Chemical name	Lincomycin
Molecular structure[a]	
Molecular formula[b]	$C_{18}H_{34}N_2O_6S$
Molecular weight[b]	406.537 g mol^{-1}
Water solubility[c]	1693 mg L^{-1} at pH 10.0 (~100% of lincomycin exists in nonionized form)
Log octanol-water partition coefficient (log K_{ow})[b]	0.20
Dissociation constant (pK_a)[b]	7.6

[a] Data from ChemSpider (http://www.chemspider.com/); [b] Data from TOXNET (http://www.toxnet.nlm.nih.gov/); [c] Water solubility was estimated using Chemicalize (https://chemicalize.com/)

Table S2. Selected properties of biochar and graphite samples.

Samples	Proximate analysis[a]			Ultimate analysis[a]				Atomic ratio				
	VM[b]	Ash	FC[c]	C	O	H	N	H/C	(O+N)/C	SSA[d]	V_{mic}[e]	ZP[f]
	%	%	%	%	%	%	%			m^2g^{-1}	cm^3g^{-1}	mV
BM300	55.5	7.7	36.8	60.6	26.6	4.9	1.3	0.97	0.35	132	0.08	-54 ± 4
BM400	37.0	9.4	53.7	68.5	17.4	3.5	1.2	0.61	0.21	168	0.09	-50 ± 3
BM500	30.5	10.4	59.2	74.1	17.4	2.6	1.1	0.42	0.19	206	0.10	-58 ± 2
BM600	30.0	10.6	59.4	76.0	14.3	1.8	0.8	0.28	0.15	271	0.12	-57 ± 4
DM300	45.4	10.1	44.5	61.5	22.6	4.5	1.6	0.88	0.30	118	0.07	-61 ± 2
DM400	39.1	11.5	49.5	67.1	16.8	3.3	1.4	0.59	0.21	156	0.08	-58 ± 1
DM600	30.7	12.6	56.6	75.2	11.6	2.0	1.3	0.32	0.13	232	0.11	-63 ± 2
PM300	46.8	46.7	6.5	31.9	16.9	2.2	2.3	0.83	0.46	49.4	0.03	-45 ± 2
PM400	43.8	51.7	4.5	32.1	14.3	0.7	1.2	0.26	0.37	45.0	0.03	-48 ± 2
PM500	43.2	52.6	4.2	27.8	17.9	0.5	1.1	0.22	0.52	55.7	0.03	-43 ± 1
PM600	44.2	55.8	0.0	28.7	14.3	0.4	0.9	0.17	0.40	49.1	0.02	-43 ± 2
RDM500	33.0	32.0	35.0	51.2	n/a[g]	n/a	2.1	n/a	n/a	118	0.06	-52 ± 3
DDM500	42.7	14.7	42.6	59.4	n/a	n/a	2.6	n/a	n/a	116	0.06	-60 ± 3
DDM600	39.4	18.8	41.7	62.8	n/a	n/a	2.2	n/a	n/a	192	0.09	-58 ± 3
CDM500	33.0	50.1	16.9	37.8	n/a	n/a	2.0	n/a	n/a	93.2	0.05	-50 ± 3
CDMW500	25.7	58.5	15.8	74.0	n/a	n/a	0.6	n/a	n/a	135	0.06	-56 ± 3
WW500	26.9	10.9	62.1	85.9	n/a	n/a	0.4	n/a	n/a	256	0.12	-64 ± 5
Graphite	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	-60 ± 1

(continued on next page)

Table S2. (continued)

Samples	Total elemental analysis[a]									
	P	K	S	Ca	Mg	Na	Fe	Mn	Zn	Si
	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$	$mgkg^{-1}$
BM300	3014	20017	1102	9412	3952	2712	376	137	162	213
BM400	3119	28939	859	10088	4841	3089	256	141	165	239
BM500	3115	33477	928	9432	4925	3518	267	146	167	613
BM600	2952	35820	1023	9386	5071	2937	311	165	193	146
DM300	1152	8986	1799	11094	3934	3270	208	52	90	115
DM400	1466	10345	1484	12808	4258	3569	305	53	87	112
DM600	2433	13236	1630	13997	5366	4538	398	98	114	310
PM300	26414	40013	4714	157531	8914	3868	1779	450	515	120
PM400	17957	28109	2983	265729	7164	3209	1276	397	352	n/d[h]
PM500	30555	48616	4593	204205	10436	4537	2034	566	601	n/d
PM600	23596	36775	3429	242788	8769	3457	1522	466	595	n/d
RDM500	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DDM500	5649	14937	1880	18505	8498	3861	2371	162	224	n/d
DDM600	8269	20852	2863	26518	11744	5051	2356	191	200	n/d
CDM500	6011	12824	2155	38388	12534	1219	9119	542	172	198
CDMW500	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
WW500	270	1573	193	5427	1267	311	4208	270	93	163
Graphite	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

[a] Data adapted from Enders et al.,2012 and Rajkovich et al., 2012.; [b] VM: volatile matter; [c] FC: fixed carbon; [d] SSA: specific surface area, measured by the Langmuir equation; [e] V_{mic}: micropore volume, calculated using Dubinin-Astakhov equation; [f] ZP: zeta potential, sorbent suspension were measured at pH 10 in 0.02 M ionic strength of background solution (6.7 mM NaCl, 2.5 mM Na_2CO_3, 2.5 mM $NaHCO_3$, and 200 mg L^{-1} NaN_3); [g] n/a: not available; [h]n/d: not detectable.

Table S3. Fitted parameters of the intraparticle diffusion model for the long-term sorption kinetics of lincomycin by the biochars.[a]

Samples	t_{ref}	k_{id}	C_{id}	R_{id}	R^2	RMSE
BM300	30	166 ± 6 a	90.6 ± 18.3 c	0.903 ± 0.008 a	0.940	72.0
BM400	180	61.7 ± 0.7 b	137 ± 4 b	0.852 ± 0.001 c	0.989	27.0
BM500	365	43.2 ± 0.2 c	115 ± 2 bc	0.876 ± 0.001 b	0.998	11.3
BM600	180	55.3 ± 0.4 b	180 ± 2 a	0.801 ± 0.001 d	0.996	14.3
DM300	90	109 ± 3 a	53.5 ± 15.1 c	0.946 ± 0.007 a	0.944	80.1
DM400	300	50.5 ± 0.8 c	145 ± 7 b	0.847 ± 0.002 b	0.975	47.4
DM600	90	88.6 ± 1.8 b	205 ± 9 a	0.789 ± 0.003 c	0.972	45.2
PM300	240	54.1 ± 0.7 a	68.6 ± 5.3 c	0.924 ± 0.001 a	0.984	34.8
PM400	365	25.3 ± 0.4 d	39.0 ± 3.8 d	0.928 ± 0.001 a	0.975	26.6
PM500	365	35.1 ± 0.3 c	162 ± 3 b	0.807 ± 0.001 b	0.993	19.0
PM600	180	49.4 ± 0.4 b	262 ± 3 a	0.719 ± 0.001 c	0.994	16.3
RDM500	180	62.1 ± 0.9 a	162 ± 6 c	0.829 ± 0.002 b	0.983	33.8
DDM500	180	62.9 ± 1 a	209 ± 6 b	0.789 ± 0.002 c	0.982	35.5
DDM600	180	44.8 ± 0.8 ce	339 ± 5 a	0.625 ± 0.002 e	0.977	28.3
CDM500	365	42.4 ± 0.3 e	124 ± 3 d	0.864 ± 0.001 a	0.994	21.9
CDMW500	300	47.5 ± 0.6 bc	162 ± 5 c	0.824 ± 0.001 b	0.987	32.3
WW500	240	48.4 ± 0.5 b	211 ± 4 b	0.768 ± 0.001 d	0.989	26.2

[a] t_{ref} (day) the longest time used when fitting the intraparticle diffusion model; k_{id} (μg g^{-1} $day^{-0.5}$): the intraparticle diffusion rate constant; C_{id} (μg g^{-1}): the intercept constant; and R_{id}: the intraparticle diffusion factor. Means with different small letters in the same column are significantly different ($p < 0.05$, one-way ANOVA with post-hoc Tukey test).

Table S4. Fitted parameters of the Freundlich model for quasi-equilibrium sorption isotherms of lincomycin on the biochars at 1, 7, 30, and 365 days. [a]

Samples	K_F				N			
	1-d	7-d	30-d	365-d	1-d	7-d	30-d	365-d
BM300	1.49 ± 0.22	30.3 ± 1.9	237 ± 8	n/a	0.727 ± 0.024 a	0.554 ± 0.012 b	0.424 ± 0.012 c	n/a
BM400	1.64 ± 0.24	5.54 ± 0.7	10.4 ± 1.7	454 ± 11	0.691 ± 0.023 a	0.626 ± 0.021 a	0.572 ± 0.027 a	0.29 ± 0.012 c
BM500	4.54 ± 0.77	7.21 ± 0.48	12.2 ± 1.1	73 ± 5.1	0.556 ± 0.027 b	0.524 ± 0.011 b	0.514 ± 0.015 b	0.483 ± 0.015 a
BM600	7.57 ± 0.61	16.4 ± 1.2	26.9 ± 1.7	282 ± 12	0.51 ± 0.013 b	0.48 ± 0.012 c	0.46 ± 0.011 c	0.325 ± 0.013 b
DM300	0.827 ± 0.186	22 ± 1.9	65.9 ± 6.6	n/a	0.69 ± 0.035 a	0.513 ± 0.015 b	0.459 ± 0.021 b	n/a
DM400	2.51 ± 0.52	4.1 ± 0.42	13.6 ± 1	146 ± 8	0.609 ± 0.031 b	0.59 ± 0.016 a	0.537 ± 0.013 a	0.48 ± 0.016
DM600	10.3 ± 1.3	38 ± 3.4	104 ± 5	n/a	0.483 ± 0.021 c	0.397 ± 0.015 c	0.369 ± 0.009 c	n/a
PM300	1.39 ± 0.24	4.68 ± 0.55	8.37 ± 0.76	215 ± 8	0.688 ± 0.027 a	0.599 ± 0.019 a	0.552 ± 0.015 a	0.407 ± 0.012 b
PM400	1.21 ± 0.23	3.22 ± 0.49	6.44 ± 0.5	20.5 ± 1.3	0.559 ± 0.029 b	0.531 ± 0.024 b	0.531 ± 0.012 a	0.524 ± 0.011 a
PM500	4.86 ± 0.54	11.2 ± 1	19.5 ± 1.3	89.7 ± 6.1	0.541 ± 0.018 bc	0.49 ± 0.014 bc	0.476 ± 0.012 b	0.402 ± 0.014 b
PM600	12.5 ± 1.5	18.9 ± 1.2	45.6 ± 3.7	312 ± 13	0.493 ± 0.02 c	0.479 ± 0.011 c	0.414 ± 0.015 c	0.348 ± 0.015 c
RDM500	6.05 ± 0.93	14.3 ± 1.6	29.4 ± 2.4	359 ± 12	0.519 ± 0.025 a	0.479 ± 0.018 bc	0.456 ± 0.014 b	0.367 ± 0.015 c
DDM500	6.76 ± 0.96	12.9 ± 0.9	38.2 ± 3.6	n/a	0.554 ± 0.023 a	0.513 ± 0.011 ab	0.413 ± 0.016 c	n/a
DDM600	15.4 ± 1.7	22.7 ± 1.7	46.4 ± 2.6	302 ± 11	0.482 ± 0.018 a	0.479 ± 0.013 bc	0.435 ± 0.01 bc	0.34 ± 0.013 c
CDM500	3.25 ± 0.73	8.3 ± 0.76	14.2 ± 1.1	77.1 ± 7	0.543 ± 0.035 a	0.523 ± 0.015 a	0.516 ± 0.013 a	0.478 ± 0.02 a
CDMW500	4.1 ± 0.79	9.38 ± 0.9	19.4 ± 2	127 ± 9	0.54 ± 0.03 a	0.511 ± 0.016 ab	0.498 ± 0.017 a	0.434 ± 0.018 ab
WW500	5.66 ± 0.95	19.8 ± 1.9	40.2 ± 3.4	187 ± 10	0.525 ± 0.027 a	0.438 ± 0.016 c	0.415 ± 0.015 c	0.403 ± 0.016 b

(continued on next page)

Table S4. (continued)

Samples	R^2				RMSE				K_d (C_w = 1 μg g^{-1})			
	1-d	7-d	30-d	365-d	1-d	7-d	30-d	365-d	1-d	7-d	30-d	365-d
BM300	0.945	0.974	0.955	n/a	14.2	36.4	68.2	n/a	1.49 ± 0.22 c	30.3 ± 1.9 a	237 ± 8 a	n/a
BM400	0.942	0.943	0.893	0.92	12.7	24.2	41	82.1	1.64 ± 0.24 c	5.54 ± 0.7 c	10.4 ± 1.7 c	454 ± 11 c
BM500	0.874	0.976	0.952	0.958	20.2	10.4	22.3	56.2	4.54 ± 0.77 b	7.21 ± 0.48 c	12.2 ± 1.1 c	73 ± 5.1 b
BM600	0.961	0.962	0.971	0.924	12.5	20.8	24.4	76.9	7.57 ± 0.61 a	16.4 ± 1.2 b	26.9 ± 1.7 b	282 ± 12 a
DM300	0.873	0.951	0.887	n/a	10.3	36	85.6	n/a	0.827 ± 0.186 c	22 ± 1.9 b	65.9 ± 6.6 b	n/a
DM400	0.854	0.957	0.969	0.957	18.1	12.8	22	59.2	2.51 ± 0.52 bc	4.1 ± 0.42 c	13.6 ± 1 c	146 ± 8
DM600	0.895	0.915	0.966	n/a	23.5	40.3	45.4	n/a	10.3 ± 1.3 a	38 ± 3.4 a	104 ± 5 a	n/a
PM300	0.922	0.946	0.959	0.957	12.7	17.5	18.5	65.2	1.39 ± 0.24 c	4.68 ± 0.55 c	8.37 ± 0.76 c	215 ± 8 b
PM400	0.858	0.889	0.968	0.978	6.21	11.5	11.4	23.9	1.21 ± 0.23 c	3.22 ± 0.49 c	6.44 ± 0.5 c	20.5 ± 1.3 d
PM500	0.939	0.952	0.966	0.929	13	17.7	22.2	67.5	4.86 ± 0.54 b	11.2 ± 1 b	19.5 ± 1.3 b	89.7 ± 6.1 c
PM600	0.907	0.971	0.931	0.914	28.2	20.4	45.7	84.9	12.5 ± 1.5 a	18.9 ± 1.2 a	45.6 ± 3.7 a	312 ± 13 a
RDM500	0.876	0.919	0.946	0.912	20	27.4	35.3	86.3	6.05 ± 0.93 bc	14.3 ± 1.6 b	29.4 ± 2.4 c	359 ± 12 a
DDM500	0.905	0.973	0.922	n/a	24.3	17.2	42.7	n/a	6.76 ± 0.96 b	12.9 ± 0.9 bc	38.2 ± 3.6 b	n/a
DDM600	0.917	0.957	0.97	0.915	29.9	28.8	33.3	92.6	15.4 ± 1.7 a	22.7 ± 1.7 a	46.4 ± 2.6 a	302 ± 11 b
CDM500	0.791	0.954	0.962	0.915	17.9	16.4	22.6	81.5	3.25 ± 0.73 c	8.3 ± 0.76 c	14.2 ± 1.1 d	77.1 ± 7 e
CDMW500	0.834	0.947	0.935	0.93	19	18.2	34.6	79.3	4.1 ± 0.79 bc	9.38 ± 0.9 c	19.4 ± 2 d	127 ± 9 d
WW500	0.86	0.926	0.927	0.915	21	26.6	43.1	79.9	5.66 ± 0.95 bc	19.8 ± 1.9 a	40.2 ± 3.4 ab	187 ± 10 c

[a] K_F (μg^{1-N} g^{-1} L^N): Freundlich sorption coefficient; N (dimensionless): Freundlich nonlinearity factor; K_d (L g^{-1}): sorption distribution coefficient; C_w (μg L^{-1}) is the dissolved lincomycin concentration in the solution phase; and n/a: fitted parameters were not available because the concentrations of lincomycin in solution were below detection limit. Means with different small letters in the same column are significantly different ($p < 0.05$, one-way ANOVA with post-hoc Tukey test).

Table S5. Fitted parameters of the intraparticle diffusion model for the sorption kinetics of lincomycin by woodchip waste biochar. [a]

Samples	t_{ref}	k_{id}	C_{id}	R_{id}	R^2	RMSE
WW500+DI	60	55.2 ± 0.4 a	178 ± 1.8 a	0.705 ± 0.001 b	0.997	7.80
WW500+DOC(BM300)	60	13.3 ± 1.2 d	80.3 ± 5.4 b	0.535 ± 0.0014 e	0.678	23.3
WW500+DOC(DM300)	60	29.1 ± 0.9 b	70.5 ± 3.9 b	0.767 ± 0.006 a	0.951	16.8
WW500+DOC(PM300)	60	15.0 ± 1.2 d	71.1 ± 5.2 b	0.598 ± 0.015 d	0.743	22.5
WW500+DOC(DDM500)	60	23.1 ± 0.9 c	85.6 ± 3.7 b	0.648 ± 0.007 c	0.931	16.0

[a] t_{ref} (day) the longest time used when fitting the intraparticle diffusion model; k_{id} (μg g^{-1} $day^{-0.5}$): the intraparticle diffusion rate constant; C_{id} (μg g^{-1}): the intercept constant; and R_{id}: the intraparticle diffusion factor. Means with different small letters in the same column are significant different ($p < 0.05$, one-way ANOVA with post-hoc Tukey test).

Table S6. Fitted parameters of the intraparticle diffusion model for the sorption kinetics of lincomycin by raw-, DI-water-washed, and 0.01M-NaOH-washed biochars. [a]

Samples	t_{ref}	k_{id}	C_{id}	R_{id}	R^2	RMSE
BM300-Raw	30	160 ± 4 b	87.9 ± 13.8 c	0.904 ± 0.003 a	0.968	47.1
BM300-DI	15	166 ± 1 b	285 ± 1 b	0.694 ± 0.001 b	1.000	3.56
BM300-NaOH	7	176 ± 5 a	527 ± 10 a	0.460 ± 0.003 c	0.985	18.7
DM300-Raw	60	113 ± 2 c	49.8 ± 8.0 c	0.945 ± 0.004 a	0.984	34.6
DM300-DI	30	148 ± 2 b	99.1 ± 7.6 b	0.894 ± 0.005 b	0.990	24.1
DM300-NaOH	10	172 ± 1 a	381 ± 1 a	0.587 ± 0.001 c	1.000	3.26
PM300-Raw	60	51.3 ± 1.5 b	83.1 ± 2.1 b	0.831 ± 0.002 a	0.995	8.93
PM300-DI	60	68.1 ± 1.5 a	131 ± 6 a	0.811 ± 0.004 b	0.976	25.4
DDM500-Raw	60	74.1 ± 0.8 b	164 ± 3 b	0.781 ± 0.002 b	0.994	13.8
DDM500-DI	60	98.5 ± 0.5 a	191 ± 2 a	0.800 ± 0.001 a	0.999	9.05
BM600-Raw	60	53.8 ± 0.6 b	174 ± 3 b	0.710 ± 0.002 a	0.993	11.0
BM600-DI	60	52.2 ± 0.9 b	175 ± 4 b	0.705 ± 0.003 a	0.983	16.3
BM600-NaOH	60	55.9 ± 0.5 a	203 ± 2 a	0.685 ± 0.002 b	0.996	8.48

[a] t_{ref} (day) the longest time used when fitting the intraparticle diffusion model; k_{id} (μg g^{-1} $day^{-0.5}$): the intraparticle diffusion rate constant; C_{id} (μg g^{-1}): the intercept constant; and R_{id}: the intraparticle diffusion factor. Means with different small letters in the same column are significantly different ($p < 0.05$, one-way ANOVA with post-hoc Tukey test).

References for Supplementary Material

Chuang, Y.H., Zhang, Y., Zhang, W., Boyd, S.A., Li, H., 2015. Comparison of accelerated solvent extraction and quick, easy, cheap, effective, rugged and safe method for extraction and determination of pharmaceuticals in vegetables. J. Chromatogr. A 1404, 1-9.

Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. Bioresour. Technol. 114, 644-653.

Liu, C.H., Chu, W.Y., Li, H., Boyd, S.A., Teppen, B.J., Mao, J.D., Lehmann, J., Zhang, W., 2019. Quantification and characterization of dissolved organic carbon from biochars. Geoderma 335, 161-169.

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., Lehmann, J., 2011. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. Biol. Fertil. Soils 48(3), 271-284.

Sigmund, G., Huffer, T., Hofmann, T., Kah, M., 2017. Biochar total surface area and total pore volume determined by N_2 and CO_2 physisorption are strongly influenced by degassing temperature. Sci. Total Environ. 580, 770-775.