Supplemental Material for

Sorption of lincomycin by manure-derived biochars from water

Cheng-Hua Liu [1, 2], Ya-Hui Chuang [1], Hui Li [1], Brian J. Teppen [1], Stephen A. Boyd [1], Javier M. Gonzalez [3], Cliff T. Johnston [4], Johannes Lehmann [5], Wei Zhang [1, 2, *]

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

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

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

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

[5] Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, United States

* Corresponding Author. 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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Supplemental Methods

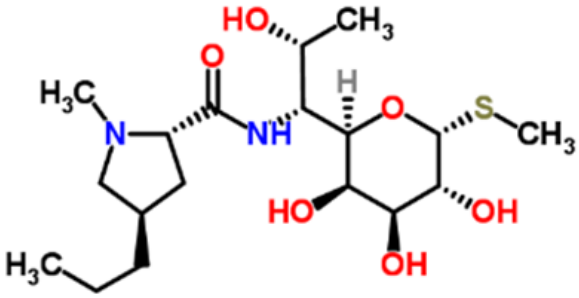
Zeta Potential Measurement

Zeta potential of biochar particles was measured with the Malvern Zetasizer Nano-ZS equipped with a MPT-2 autotitrator (Malvern Instruments, Worcestershire, UK). To generate biochar colloid suspension for isoelectric point (pH_{IEP}) measurement, 10 mg biochar (particle size < 75 μm) was mixed with 50 mL DI water in a polyethylene centrifuge tube and then sonicated for 30 min. After sonication, top 10 mL of biochar suspension was withdrawn and then titrated with 0.1 M HCl or NaOH titrant from pH 10 to 2 using the autotitrator, and the corresponding zeta potential at each pH was measured by the Zetasizer Nano-ZS. The pH_{IEP} value was determined at the pH where the zeta potential is zero. Additionally, zeta potential for biochar suspensions of 1-day or 180-day water exposure was also determined by the zetasizer.

LC-MS/MS Analytical Procedure

Lincomycin concentrations in the solution were determined by a Shimadzu Prominence high-performance liquid chromatograph coupled to an Applied Biosystems Sciex 3200 triple quadrupole mass spectrometer (LC-MS/MS). A Gemini 5u C18 110A 50×2.00 mm 5 μm column was used. The mobile phase consisted of water (A) and 1:1 (v/v) acetonitrile-methanol mixture (B) with A and B both containing 0.3% formic acid. Gradient conditions were 0 % to 40 % B in 0 to 1 minute, 40 % to 70% B in 1 to 2 minutes, 70 % – 80 % B in 2 to 3 minutes, 80 % to 100 % B in 3 to 3.5 minutes, and held for 0.5 minutes at a flow rate of 0.35 mL/min. Injection volume was 10 μL. The tandem quadrupole MS was used with an electrospray ionization (ESI) and positive ion mode. Lincomycin was detected and quantified using a multiple reaction monitoring mode with a precursor/product transition of 407.2/126.2. The retention time and instrument detection limit of lincomycin was 2.37 min and 0.2 pg.

Table S1. Chemical and physical properties of lincomycin[†]

Properties	Lincomycin
Molecular structure[‡]	
Molecular Formula[§]	$C_{18}H_{34}N_2O_6S$
Molecular weight[§]	406.54
pKa[§]	7.6
log K_{ow}[§]	0.20
Water solubility[§]	927 mg L^{-1} at 25 °C

[†] pKa: dissociation constant, K_{ow}: octanol/water partition coefficient; [‡] Data from ChemSpider (http://www.chemspider.com/); [§] Data from TOXNET (http://www.toxnet.nlm.nih.gov/)

Table S2. Fitted parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models for long-term sorption kinetics of lincomycin on manure-derived biochars.

Biochar	Pseudo-first-order			
	q_e ($\mu g \cdot g^{-1}$)	k_1 (day^{-1})	R^2	RMSE
BM600	937	3.11×10^{-2}	0.837	175
DM600	855	3.37×10^{-2}	0.951	187
AM600	851	3.13×10^{-2}	0.867	203
PM600	860	3.07×10^{-2}	0.837	197
	Pseudo-second-order			
	q_e ($\mu g\ g^{-1}$)	k_2 ($\mu g\ g^{-1}\ day^{-1}$)	R^2	RMSE
BM600	856	9.91×10^{-5}	0.916	144
DM600	990	1.46×10^{-4}	0.987	124
AM600	907	1.40×10^{-4}	0.959	142
PM600	852	1.13×10^{-4}	0.927	169
	Intraparticle diffusion			
	C ($\mu g \cdot g^{-1}$)	k_i ($\mu g\ g^{-0.5}\ day^{-0.5}$)	R^2	RMSE
BM600	160	52.3	0.973	34.0
DM600	212	66.2	0.965	49.7
AM600	228	54.6	0.963	42.1
PM600	216	47.0	0.972	31.2

Table S3. Fitted parameters of Langmuir and Freundlich equations for lincomycin sorption on manure-derived biochars.

Biochar	Langmuir				Freundlich			
	q_{max} ($\mu g\ g^{-1}$)	K_L ($L\ \mu g^{-1}$)	R^2	RMSE	n^{-1}	K_F ($\mu g^{(n-1)}\ g^{-1}\ L^n$)	R^2	RMSE
BM600 pH 6.6	555	1.29×10^{-2}	0.99	15	0.47	28.5	0.98	34
BM600 pH 9.9	299	7.87×10^{-3}	1.00	5.2	0.44	15.4	0.96	18
DM600 pH 6.5	605	1.40×10^{-2}	0.99	19	0.48	30.7	0.97	38
DM600 pH 10.0	372	5.68×10^{-3}	0.97	17	0.48	13.4	0.97	13
AM600 pH 6.9	697	6.18×10^{-3}	1.00	9.3	0.61	13.7	0.99	29
AM600 pH 10.0	436	4.58×10^{-3}	0.97	18	0.55	10.1	0.95	19
PM600 pH 7.3	576	2.68×10^{-3}	0.96	15	0.71	4.29	0.96	29
PM600 pH 10.4	424	3.41×10^{-3}	0.98	12	0.59	6.83	0.98	11

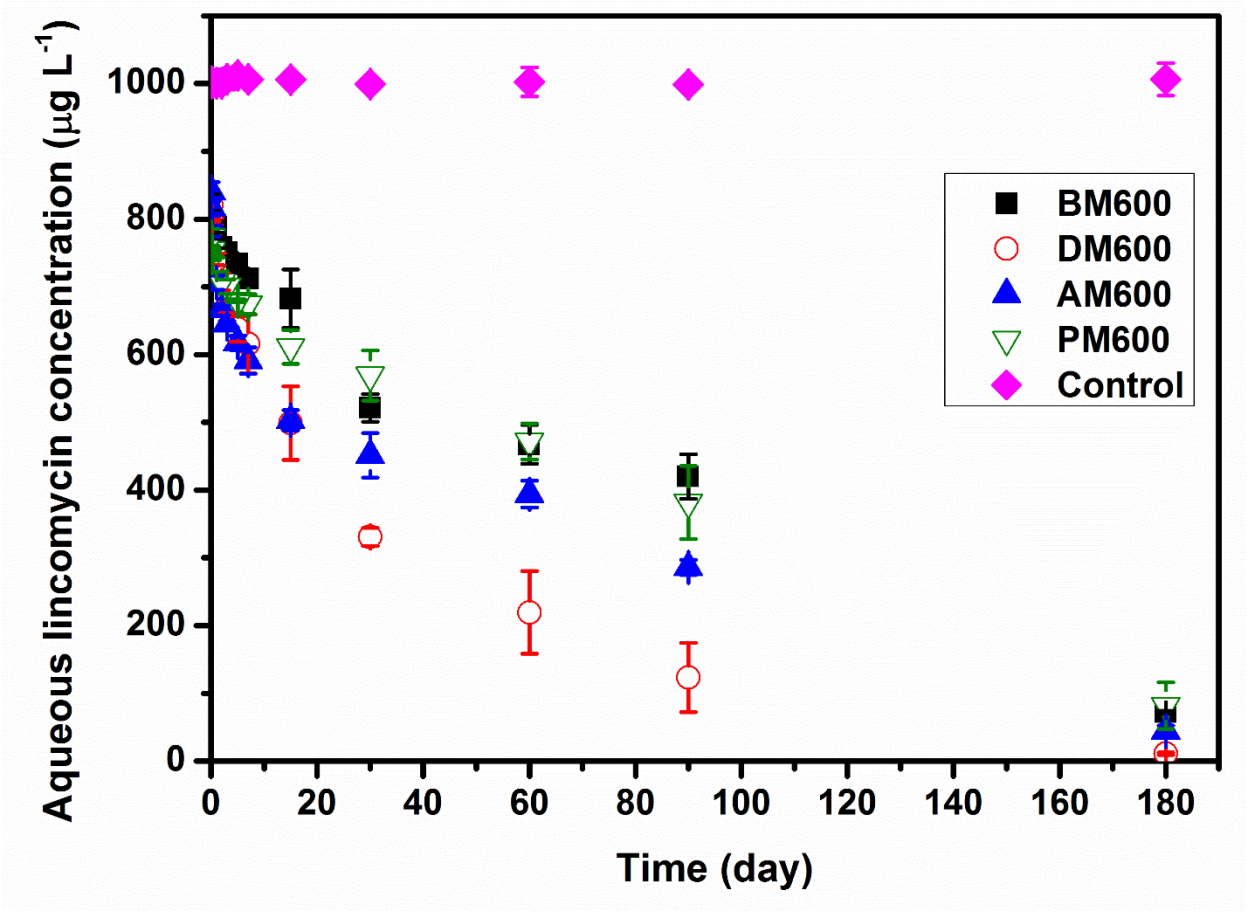


Fig S1. Lincomycin concentration versus time for lincomycin sorption kinetics experiments. Control was the biochar-free lincomycin solution.

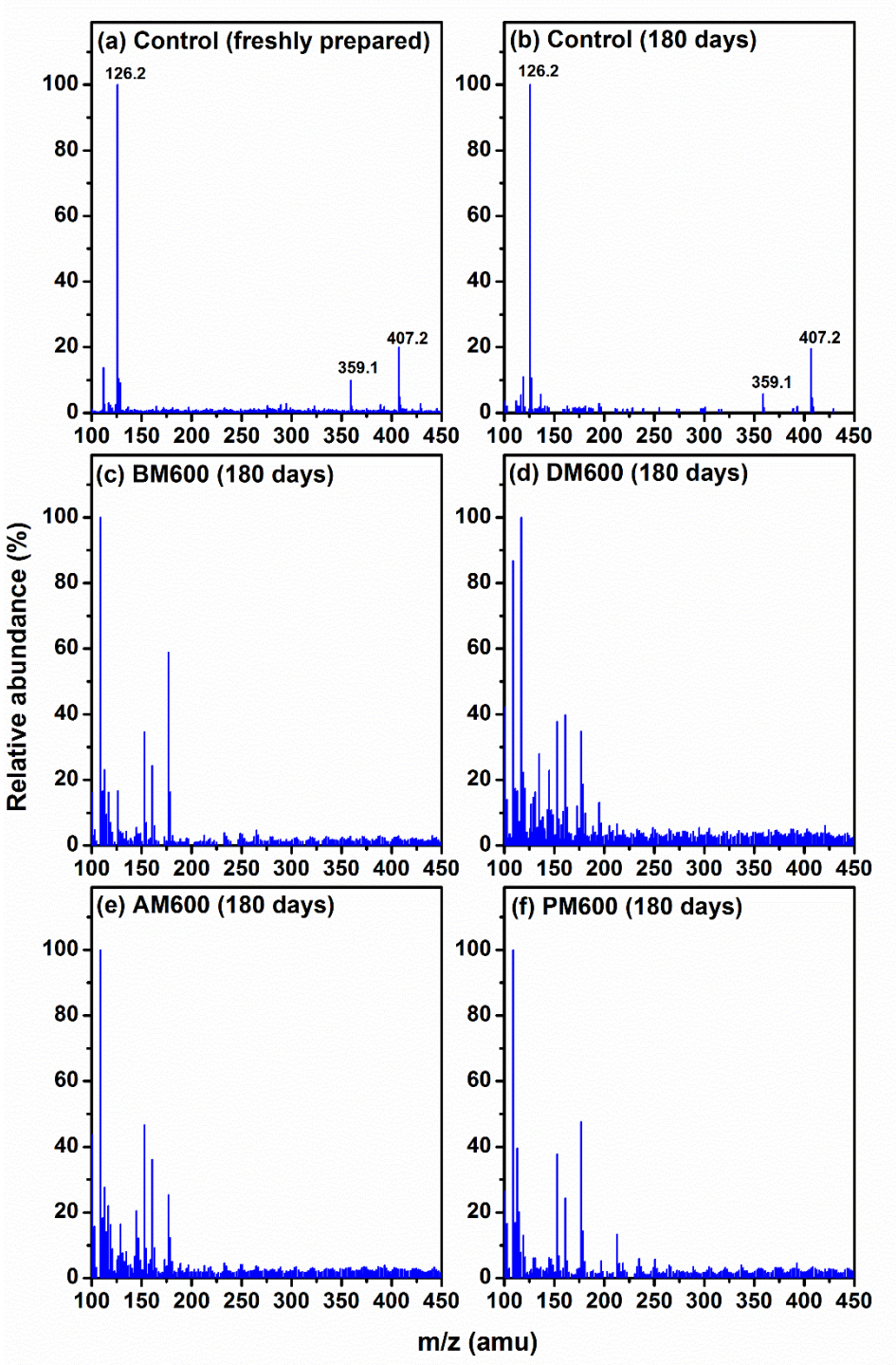


Fig S2. Precursor ion scan spectra of (a) Control (freshly prepared), (b) Control (180 days), (c) BM600 (180 days), (d) DM600 (180 days), (e) AM600 (180 days), and (f) PM600 (180days). Control was the biochar-free lincomycin solution. No degradation candidates of lincomycin was detected in long-term kinetics samples (b, d, f).

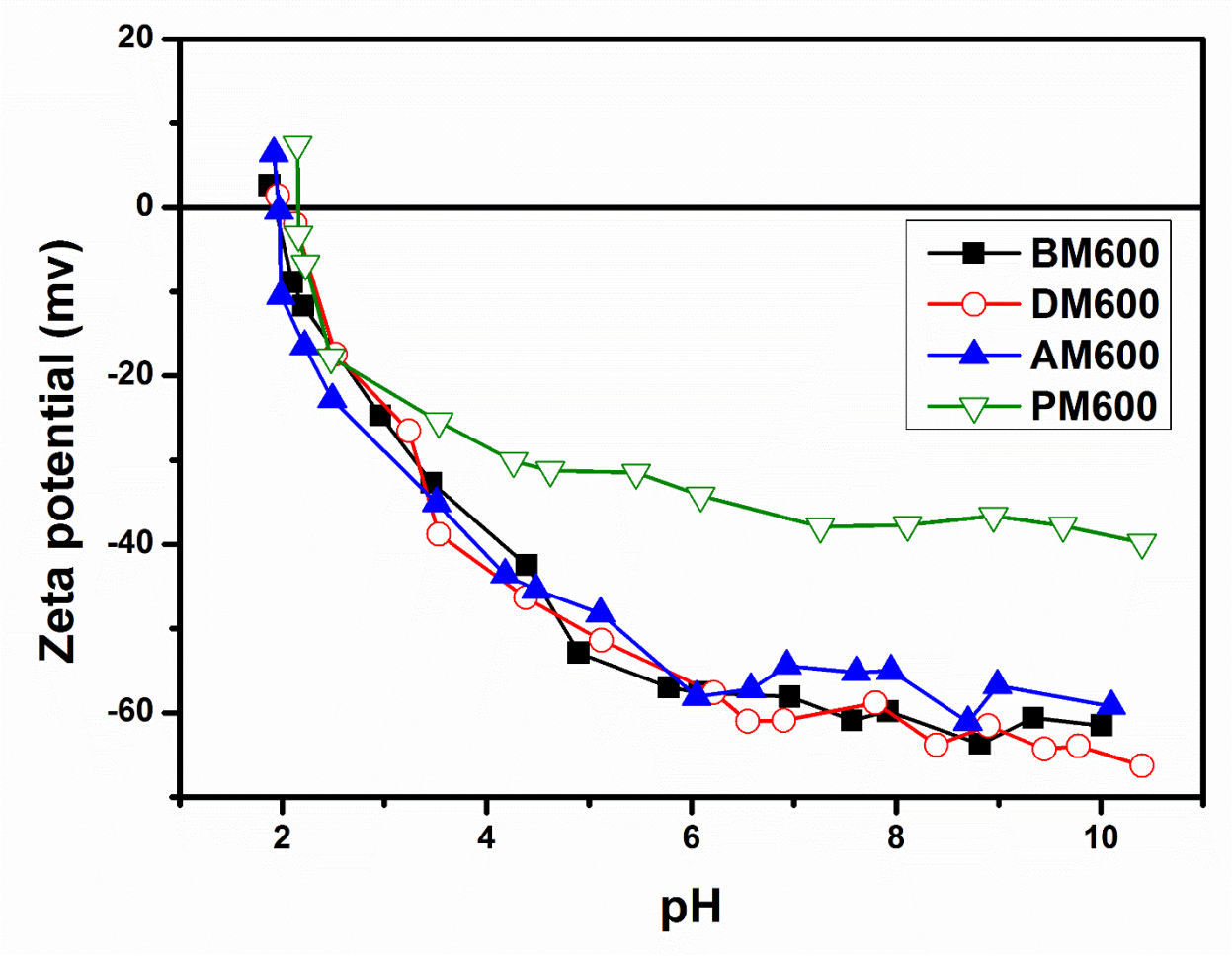


Fig S3. Zeta potential of manure-derived biochars as a function of solution pH.