Supplementary data

Facile and Economical Functionalized Hay Biochar with Dairy Effluent for Adsorption of Tetracycline

Yong-Keun Choi[†, ‡, §], Rajani Srinivasan[¶], Eunsung Kan*[, †, ‡]

[†]Department of Biological and Agricultural Engineering & Texas A&M AgriLife Research Center, Texas A&M University, 1229 North US Highway 281, Stephenville, TX 76401, USA.

[‡]Department of Wildlife, Sustainability, and Ecosystem, Tarleton State University, 1333 W. Washington, Stephenville, TX 76401, USA.

[§]Department of Biological Engineering, Konkuk University, Seoul 05029, Republic of Korea.

[¶]Department of Chemistry, Geosciences and Physics, Tarleton State University, Stephenville, TX 76401, USA.

*Corresponding author: Eunsung Kan

Texas A&M AgriLife Research Center, Stephenville, TX 76401, USA.

E-mail: eunsung.kan@ag.tamu.edu

Telephone: 1-254-968-4144

Fax: 1-254-968-3759

1. Characterization of biochar. The elemental compositions in the AF-BC and DEAF-BC were analyzed by an elemental analyzer (PerkinElmer 2400 Series II, MA, USA). The ash, volatile matter, and fixed carbon content were also determined carbon (C), hydrogen (H), and nitrogen (N) contents in the AF-BC and DEAF-BC were evaluated by an elemental analyzer (PerkinElmer 2400 Series II, MA, USA). Based on the difference of the C, N, H, and ash contents, oxygen content was calculated. The ash, volatile matter, and fixed carbon content were also determined using a muffle furnace (Sybron Termolyne Furnatrol II, Thermolyne, Dubuque, IA, USA) and a pyrolysis reactor (Multi Position Tube Furnace GSL-1100X-S, MTI Co., Richmond, Ca, USA) according to the ASTM standard D1762-84 and D5142-02a [1-3]. The element compositions (i.e. Ca, Mg, K, P, Na, Zn, Cu, Mn and Fe) of AF-BC and DEAF-BC were analyzed by ICP (Spectro Radial Modula ICP, Spectro analytical Instruments, Marlborough, MA). The morphology and elements on the surface of AF-BC and DEAF-BC were analyzed with a scanning electron microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX, Hitachi S-4800, Hitachi Co., Japan). X-ray diffraction (XRD) patterns of AF-BC and DEAF-BC were determined by Rigaku MiniFlex II (Rigaku, Japan) at a range from 2 to 72° at 1.25° min^{-1} with 0.02^{o} (2θ) step size at 30 kV and 15 mA. Crystallization were identified by comparing with the peaks of standard compounds. The measurement of Brunauer-Emmett-Teller (BET) surface area of AF-BC and DEAF-BC were performed on the basis of N_2 adsorption at 77K with Micromeritics Gemini VII 2390p (Norcross, USA). Fourier transform infrared (FTIR) of AF-BC and DEAF-BC was obtained at 400 and 4000 cm^{-1} using a Bruker Alpha FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) [3].

The pH of zero point charges ($pH_{,pzc}$) analyses were conducted as described previously [3-4]. Briefly, 50 mL of NaCl solution (0.01 M) adjusted to a range from 3.0 to 10.0 using 0.1M

of NaOH or HCl solution was placed in a 100 mL glass bottle and 0.01 g BC was added to the solution. And then, the final pH of solution was measured after 2 d incubation at 22 °C and 150 rpm. The $pH_{,pzc}$ from each set were obtained from the ΔpH (final−initial pH) = 0.

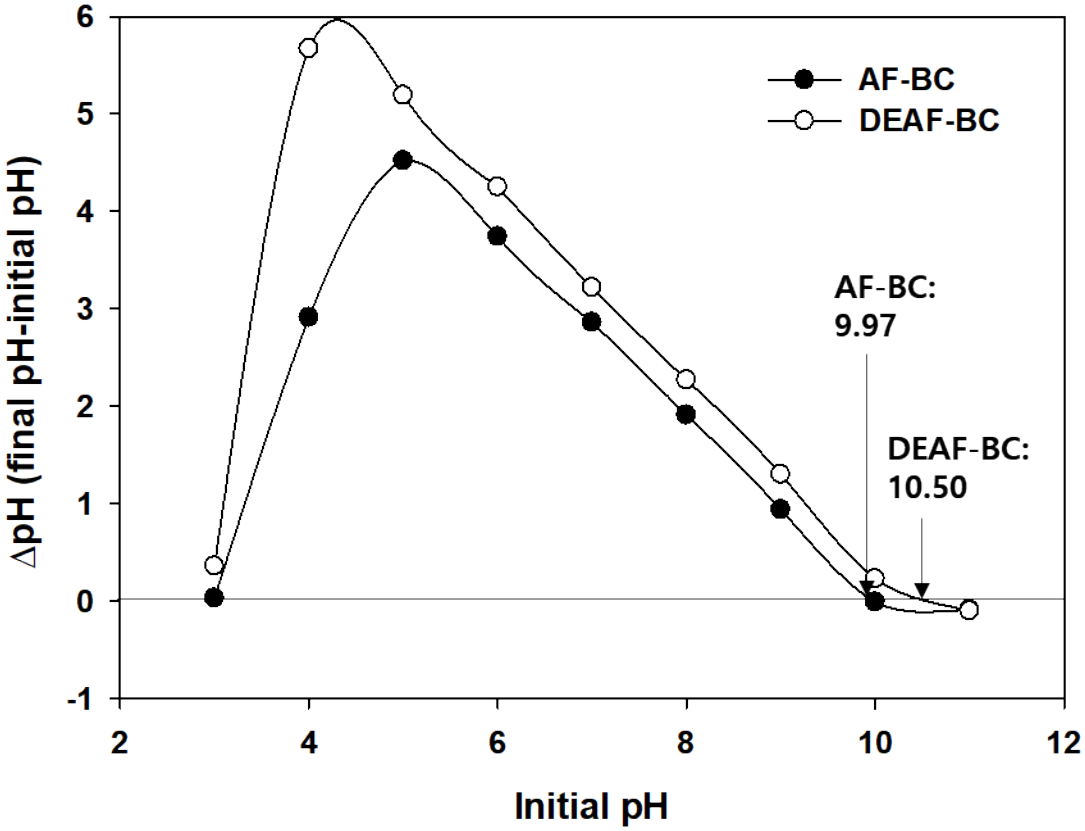

Figure S1. $pH_{,pzc}$ of AF-BC and DEAF-BC.

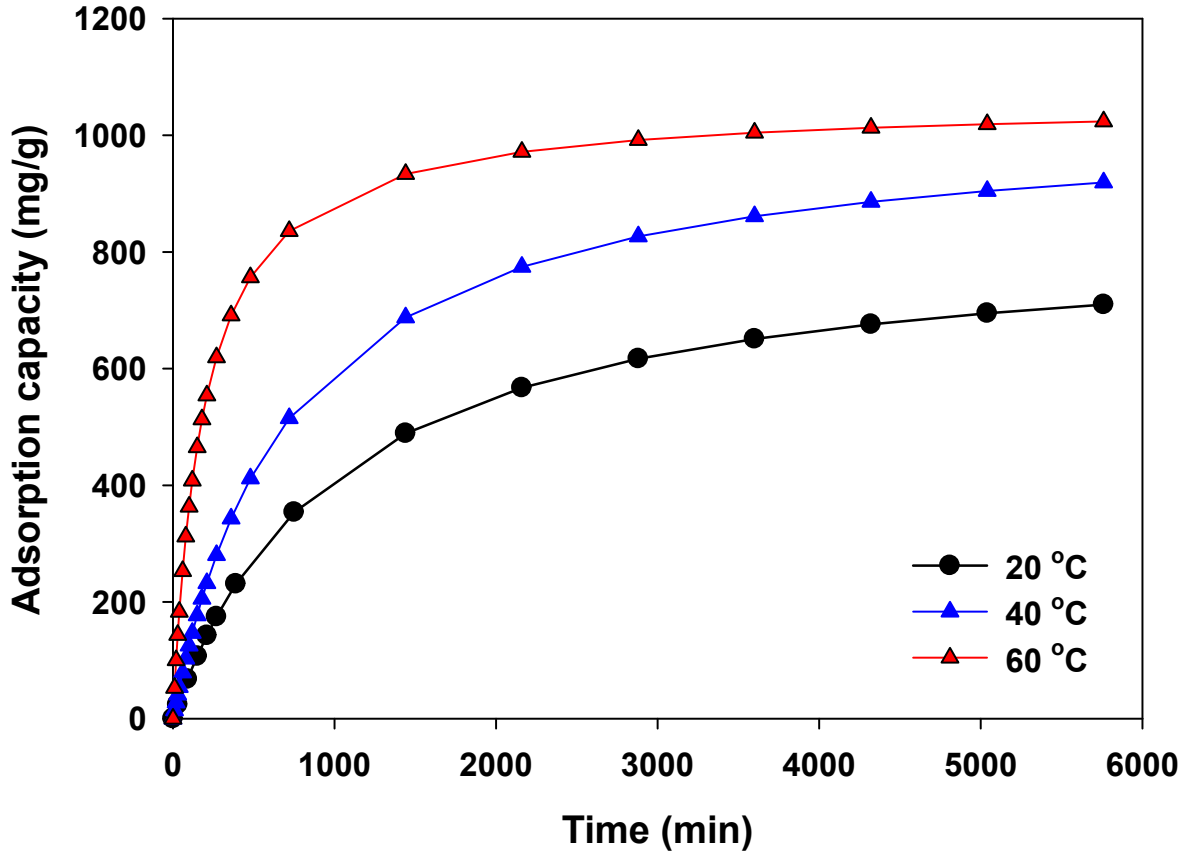

Figure S2. Adsorption of TC onto DEAF-BC at various temperatures. [Conditions] 100 mL, 100 mg/L TC, 0.01 g BC, pH = 6, 4 d. The pseudo second order model was fitted to the experimental data.

Table S1. EDX results of AF-BC and DEAF-BC

Element (%)	AF-BC	DEAF-BC
C	67.24	47.04
N	7.16	2.44
O	14.76	20.63
Na	0.66	2.56
Mg	2.23	1.82
P	1.05	7.85
K	0.76	0.68
Ca	5.95	16.37
Fe	0.19	0.61

Table S2. Surface charge of the DEAF-BC and TC adsorption at various solution pH

pH	DEAF-BC ($pH_{,pzc}$ = 10.5)	TC (pKa =3.3, 7.7, 9.7)	Interactions
pH <3.3	Positively charge dominated	Positively charge (H_4TC^+, dominated)	π-π interaction and van der waals forces
3.3<pH<7.7	Positively charge dominated	Non-charge (H_3TC^0, dominated)	π-π interaction, hydrogen bonding and van der waals forces
7.7<pH<9.7	Positively charge dominated	Negatively charge (H_2TC^-, dominated)	Electrostatic attraction
9.7<pH<10.5	Positively charge dominated	Negatively charge (HTC^{2-}, dominated)	Electrostatic attraction
pH>10.5	Negatively charge dominated	Negatively charge (HTC^{2-}, dominated)	π-π interaction and van der waals forces

Table S3. Adsorption kinetic parameters of TC onto DEAF-BC

Conc. (mg/L)	Pseudo-first order					Pseudo-second order			
	Q_e[a]	Q_e[b]	K_1	SSE	R^2	Q_e[b]	K_2	SSE	R^2
100	719.2	701.7	0.0008	46.5	0.959	835.7	0.0000017	38.7	0.967

Conc. (mg/L)	Elovich					Two-compartment first-order						
	a	b	t_o	SSE	R^2	Q_e[b]	F_{fast}	F_{slow}	K_{fast}	K_{slow}	SSE	R^2
100	3.34	0.007	40.3	62.2	0.927	762.8	0.137	0.863	175.0	0.032	15.7	0.995

Conc. (mg/L)	Liquid film diffusion				Intra-particle diffusion							
	Q_e[b]	K_{fd}	SSE	R^2	Q_e[b]	K_i	K_{i1}	K_{i2}	K_{i3}	C_i	SSE	R^2
100	701.7	0.0008	46.5	0.959	789.3	9.812	17.980	11.597	4.622	44.5	35.3	0.976

a: observed, b: calculated. Conditions: 100 mL of 100 mg/L TC, 0.01 g BC, pH = 6, 22 ^oC, 4 d.

Table S4. Adsorption isotherm parameters of TC onto DEAF-BC

Conc. (mg/L)	Langmuir			Freundlich			Temkin		
	K_L	Q_m	R^2	K_f	n_f	R^2	b_T	K_T	R^2
100	0.000008	601803	0.900	22.44	1.422	0.953	16.01	0.247	0.782

[conditions] TC solution (100 mL, 10-600 mg/L), 0.01 g BC, pH = 6, 22 ^{o}C, 5 d.

Table S5. Cations in leachate of DEAF-BC at various pH

Solution pH	Cations (mg/L)					
	Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
pH 2	ND	1.76	ND	0.58	1.94	7.88
pH 6	ND	1.13	ND	ND	0.45	2.70
pH 11	ND	21.19	ND	ND	ND	0.83

ND: not detected

[conditions] 100 mL of distilled (DI) water, 0.01 g DEAF-BC, 22 ^{o}C, 5 d

Table S6. Adsorption kinetic and isotherm models

Models	Names: Equations
Kinetic	Pseudo-first order: $Q_t = Q_e(1 - exp(-K_1 t))$
	Pseudo-second order: $Q_t = Q_e(1 - exp(-K_2 t))$
	Elovich: $Q_t = \left(\frac{1}{b}\right) lnab + \left(\frac{1}{b}\right) lnt,\ t_0 = \frac{1}{ab}$
	Intra-particle diffusion: $Q_t = K_i\sqrt{t} + C_i$
	Liquid film diffusion: $\ln(1 - F) = -K_{fd}t, F = \frac{Q_t}{Q_e}$
	Two-compartment: $\frac{Q_t}{Q_{t=\infty}} = F_{fast}(1 - exp^{-tK_{fast}}) + F_{slow}(1 - exp^{-tK_{slow}}),\ F_{fast} + F_{slow} = 1$
Isotherm	Freundlich: $Q_e = K_f C_e^{\frac{1}{nf}}$
	Langmuir: $Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}, R_L = \frac{1}{1 + K_L C_0}$
	Temkin: $Q_e = \frac{RT}{b_T} \ln(K_T C_e)$

Q_t is an adsorption capacity (mg/g) at time t (min), Q_e is an adsorption capacity (mg/g) at equilibrium time, K_1 is a rate constant of Pseudo-first order, K_2 is a rate constant of Pseudo-second order, a is a rate constant of chemisorption, b is a constant of the surface coverage, K_i is Intra-particle diffusion rate constant (mg $min^{0.5}$/g), C_i is a constant (mg/g), K_{fd} is adsorption rate constant, F_{fast} is mass fraction of fast,, F_{slow} is mass fraction of slow, K_{fast} is first order rate constant for transfer into fast (h^{-1}), K_{slow} is first order rate constant for transfer into slow (h^{-1}), and h is hour. Q_e is the amount of TC adsorbed per unit mass of adsorbent at equilibrium (mg/g), K_f is a constant to indicate adsorption capacity, C_e is the liquid-phase concentration of TC at equilibrium (mg/L), $1/n_f$ is an indicator of adsorption effectiveness, Q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/g) related to the adsorption/desorption energy, R_L is separation constant, and C_0 is the liquid-phase concentration of TC at initial (mg/L), R is universal gas constant (8.314 J/mol), T is temperature in terms of Kelvin, b_T is Temkin constant, K_T is equilibrium bond constant related to the maximum energy of bond.

(1) Standard, A., Standard test method for chemical analysis of wood charcoal. American Society for Testing and Materials, Conshohocken, PA, **2009**.

(2) Coal, A. C. D.-o.; Coke, Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures. ASTM International: **2009**.

(3) Choi, Y.-K.; Kan, E., Effects of pyrolysis temperature on the physicochemical properties of alfalfa-derived biochar for the adsorption of bisphenol A and sulfamethoxazole in water. *Chemosphere.* **2019**, *218*, 741-748.

(4) Jang, H. M.; Yoo, S.; Choi, Y.-K.; Park, S.; Kan, E., Adsorption isotherm, kinetic modeling and mechanism of tetracycline on *Pinus taeda*-derived activated biochar. *Bioresour. Technol.* 2018, *259*, 24-31.