Supplementary materials

Characterization of KOH modified biochars from different pyrolysis temperatures and enhanced adsorption of antibiotics

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The following is included as additional **Supplementary materials** for this paper.

Table S1. Non-linear forms of kinetic and isothermal models

Names	Equation
Kinetic models	
Pseudo-first order	$q_t = q_e[1 - exp(-k_1 t)]$; $h_0 = k_1 q_e$
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$; $h_0 = k_2 q_e^2$
Intraparticle diffusion	$q_t = k_{id}\sqrt{t} + C_i$
Elovich	$q_t = \frac{1}{\beta} ln(1 + \alpha\beta t)$
Isothermal models	
Freundlich	$q_e = k_F C_e^{1/nF}$
Temkin	$q_e = \frac{RT}{b_T} ln(k_T C_e)$

Note: q_t (mg • g^{-1}) is the adsorbed amount at a given time. k_1 (min^{-1}) is the rate constant of the pseudo-first order model. k_2 (g • mg^{-1} • min^{-1}) is the rate constant of the pseudo-second order model, and h_0 (mg • g^{-1} • min^{-1}) is the initial adsorption rate.α (mg • g^{-1} • min^{-1}) and β (g • mg^{-1}) are the Elovich constants. k_{id} (mg • g^{-1} • min$^{-0.5}$) and C_i (mg • g^{-1}) are the intraparticle diffusion constants. q_e (mg • g^{-1}) is the amount adsorbed at equilibrium. q_m (mg • g^{-1}) is the maximum adsorption capacity. k_F (mg • g^{-1}) and n_F are the Freundlich constants. R is the universal gas constant (8.314 J • mol^{-1} • K^{-1}), T = the absolute temperature in Kelvin (298K), and k_T (L • g^{-1}) and b_T (J • mol^{-1}) are the Temkin constants.

Table S2. Parameters of kinetic models for the adsorption of TC onto biochars

	RBC300	RBC500	RBC700	KBC300	KBC500	KBC700
$q_{m,exp}$	4.30	7.37	11.63	21.17	4.97	7.13
Pseudo-first order	**Δ qe = 18.82%**					
q_e (mg·g^{-1})	4.30	7.37	11.63	21.17	4.97	7.13
k_1 (h^{-1})	0.046	0.16	0.469	0.235	0.104	0.169
h_0 (mg·g^{-1}·h^{-1})	0.198	1.179	5.454	4.975	0.517	1.205
R^2	0.75	0.91	0.76	0.88	0.91	0.872
Δq_e (%)	35.19	12.15	12.31	12.63	16.26	15.75
Pseudo-second order	**Δ qe = 12.92%**					
q_e (mg·g^{-1})	4.13	7.28	11.59	21.01	4.87	7.05
k_2 (g·mg^{-1}·h^{-1})	0.018	0.034	0.084	0.020	0.032	0.039
h_0 (mg·g^{-1}·h^{-1})	0.307	1.749	11.284	8.828	0.759	1.938
R^2	0.89	0.95	0.90	0.97	0.97	0.95
Δq_e (%)	24.06	14.26	7.59	5.69	9.92	8.41
Elovich	**Δ qe = 13.86%**					
q_e (mg·g^{-1})	4.22	7.59	11.43	21.59	6.8	7.4
α (mg·g^{-1}·min^{-1})	1.082	19.19	5.574×10^6	754.534	3.854	34.540
β (g·mg^{-1})	1.469	1.171	1.928	0.542	1.462	1.298
R^2	0.97	0.91	0.98	0.98	0.96	0.98
Δq_e (%)	11.12	27.52	2.30	4.97	16.03	4.04

Table S3. Parameters of intraparticle diffusion for adsorption of TC onto biochars in the second stage

	Time range h	K_{id} mg • g^{-1} • $h^{-0.5}$	C_i mg • g^{-1}	R^2
RBC300	4-120 （116）	0.195	1.260	0.99
RBC500	4-24 （20）	0.630	3.064	0.99
RBC700	2-8 （6）	0.766	7.620	0.96
KBC300	4-72 （68）	0.842	12.882	0.96
KBC500	8-120 （112）	0.234	2.342	0.97
KBC700	4-24 （20）	0.354	3.644	0.99

Note: Duration time was listed in brackets.

Table S4. Parameters of the Freundlich and Temkin isotherm models

	RBC300	RBC500	RBC700	KBC300	KBC500	KBC700
Frendlich						
k_F ($mg \bullet g^{-1}$)	0.211	1.636	5.296	3.483	1.885	3.397
n_F	1.328	1.89	2.907	1.414	3.03	4.032
$1/n_F$	0.753	0.529	0.344	0.707	0.33	0.248
R^2	>0.99	0.97	0.96	0.77	0.96	0.98
Δqe (%)	4.38	7.03	6.21	20.31	4.70	2.73
Temkin						
b_T ($L \bullet g^{-1}$)	1731.9	752.5	629.4	187.8	1735.7	1670.9
k_T ($J \bullet mol^{-1}$)	0.228	0.597	2.233	0.448	1.837	6.296
R^2	0.95	0.92	0.90	0.93	0.92	0.98
Δqe (%)	12.63	11.47	11.10	10.62	7.54	2.68

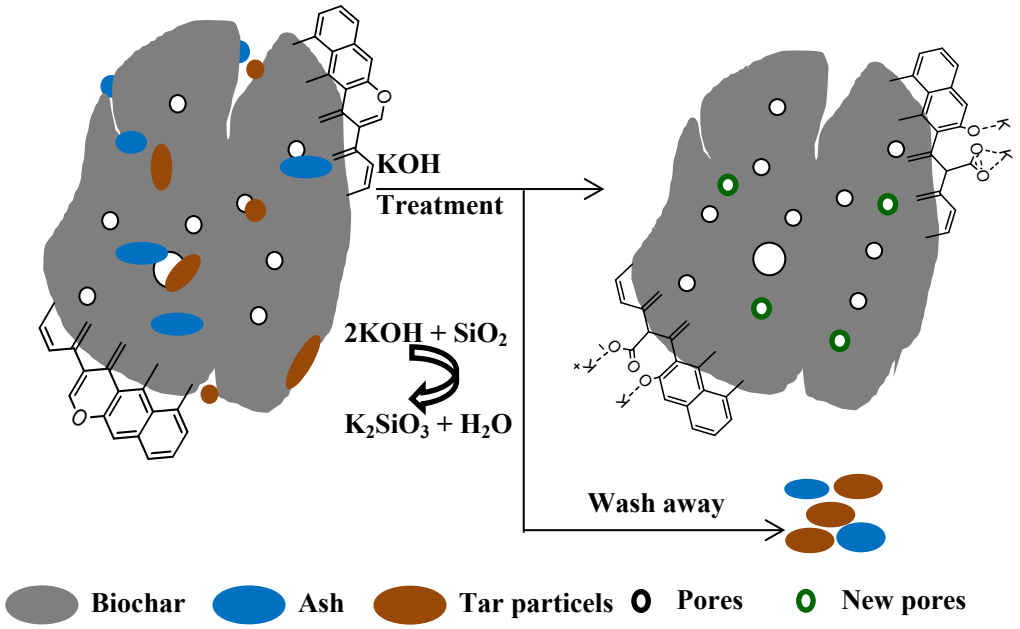

Figure S1. Schematic diagram of KOH modifying processes. **KOH modifying mechanism:** Several reactions were included in cold KOH modifying processes: (1) KOH could increase oxygen functional groups by hydrolysis reaction of biomass left.[1, 2] (2) KOH could interact with SiO_2 to form K_2SiO_3, which would flush away with water in subsequent washing process.[3] (3) tar particles and some other organic compounds were removed by defatting.[4, 5] Though these reactions, surfaces of BC would corroded and became rougher,[3, 5] and average pore diameter would enlarge.[5, 6]

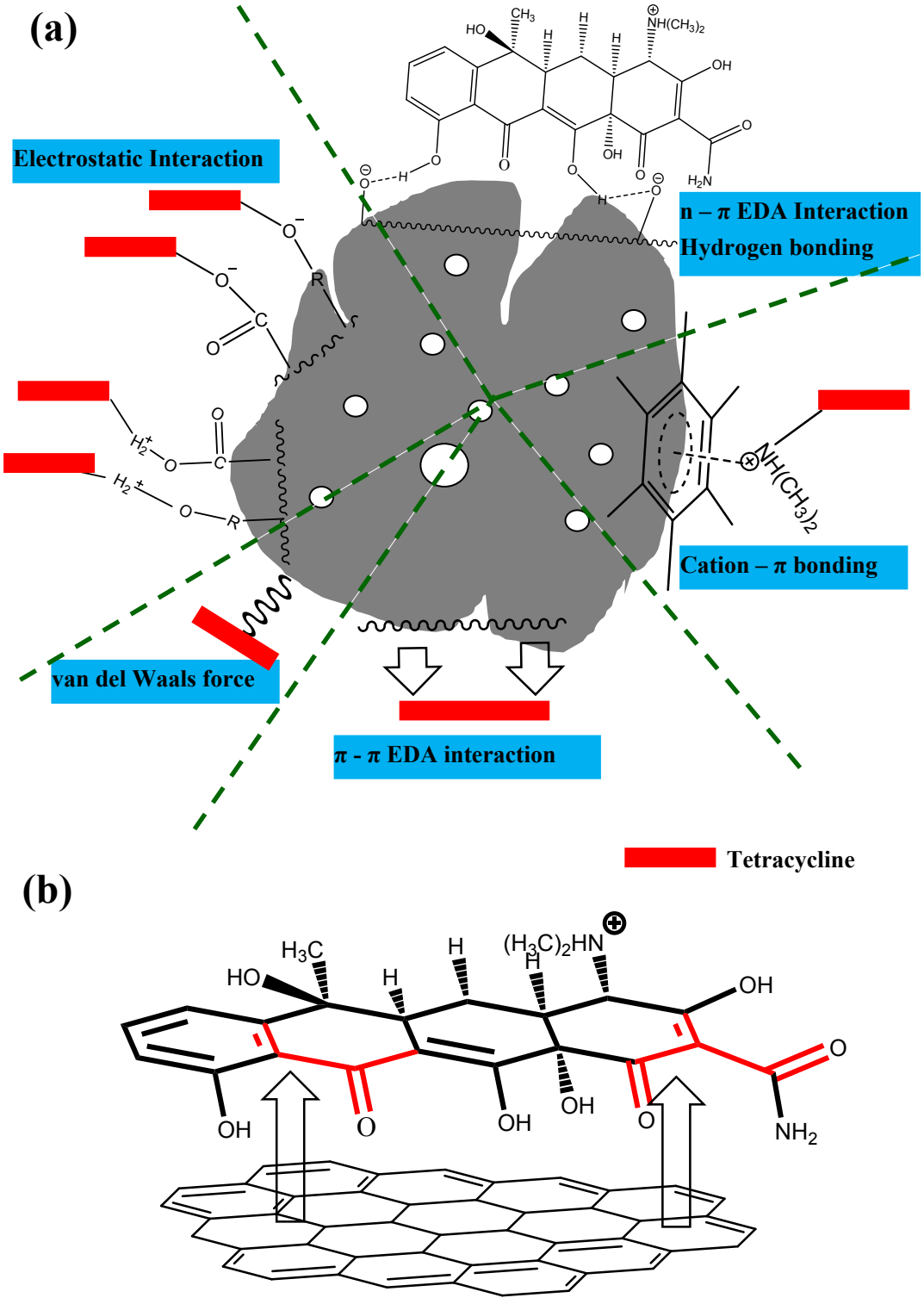

Figure S2. Schematic diagram of tetracycline adsorption onto biochar (a) and π – π EDA interaction (b). **interactions with π electron incluced in tetracycline adsorption: 1) π – π EDA interaction**: the conjugated enone structures of

tetracycline molecule function as π-electron-acceptors, and interact strongly with the graphene surface (π-electron-donor) of biochars.[7, 8] **2) n – π EDA interaction**: the interactions between the hydroxyl group or ionized moiety ($-O^-$) (n-electron donor) and conjugated enone structures of tetracycline (π -electron acceptors).[9] **3) Cation – π bonding:** the electrostatic force between the amino group of tetracycline and the permanent quadrupole of the π-electron-rich aromatic structure of graphene surface and cation-induced polarization.[7, 10]

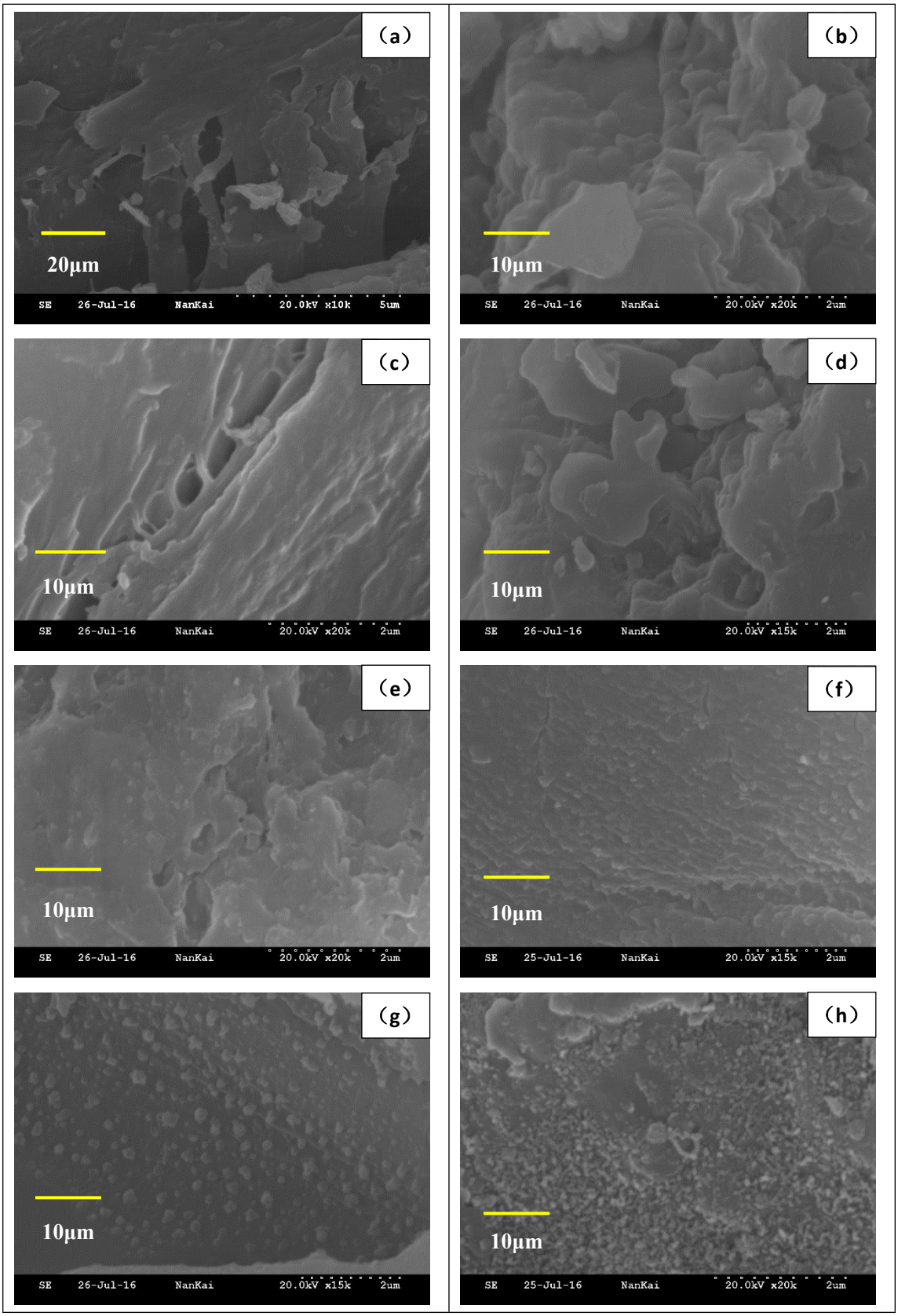

Figure S3. SEM micrographs of the surface of raw feedstock (a and b), RBC300~700 (c, e and g), and KBC300~700 (d, f and h).

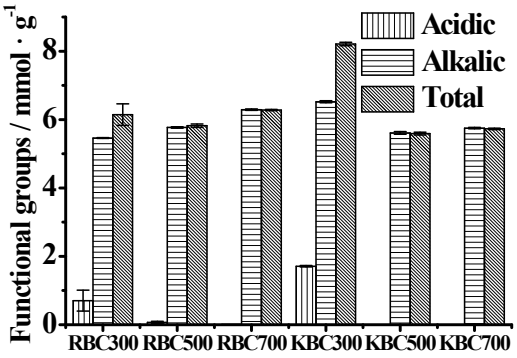

Figure S4. Surface oxygen functional groups (SOFGs) for RBCs and KBCs

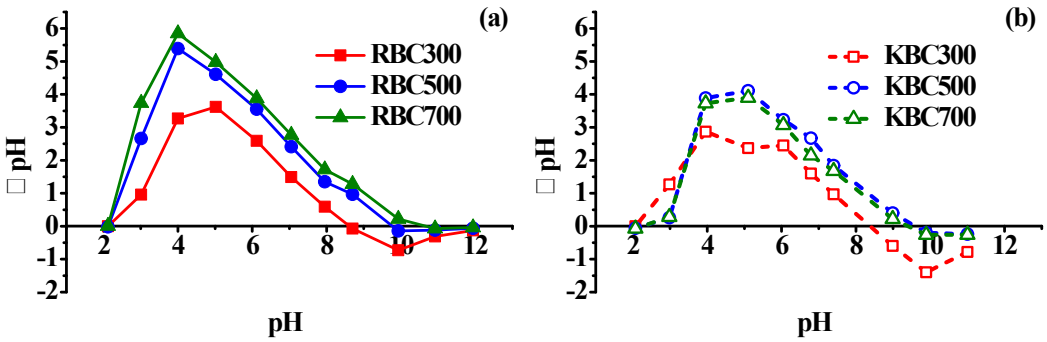

Figure S5. pH_{PZC} of RBCs (a) and KBCs (b).

Note: ΔpH was difference value of solution pH before and after equilibrium.

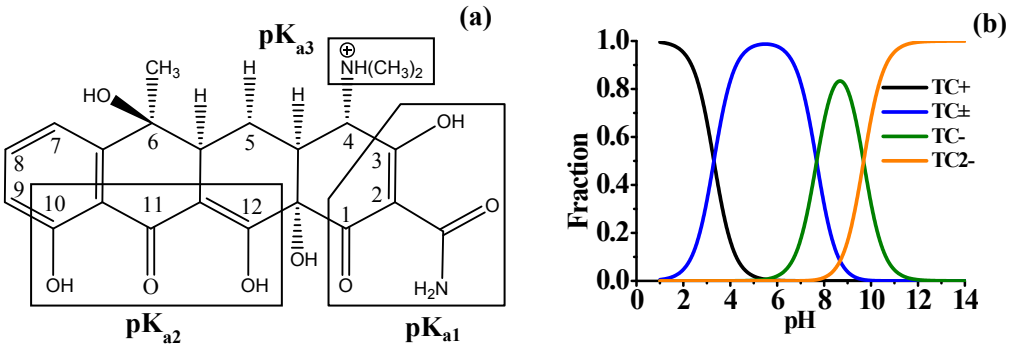

Figure S6. Molecular structure of tetracycline (a) and species distribution diagram of TC as a function of solution pH (b).

Reference

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