Supporting Information

Enhanced adsorption capacity of tetracycline on porous graphitic biochar with an ultra-large surface area

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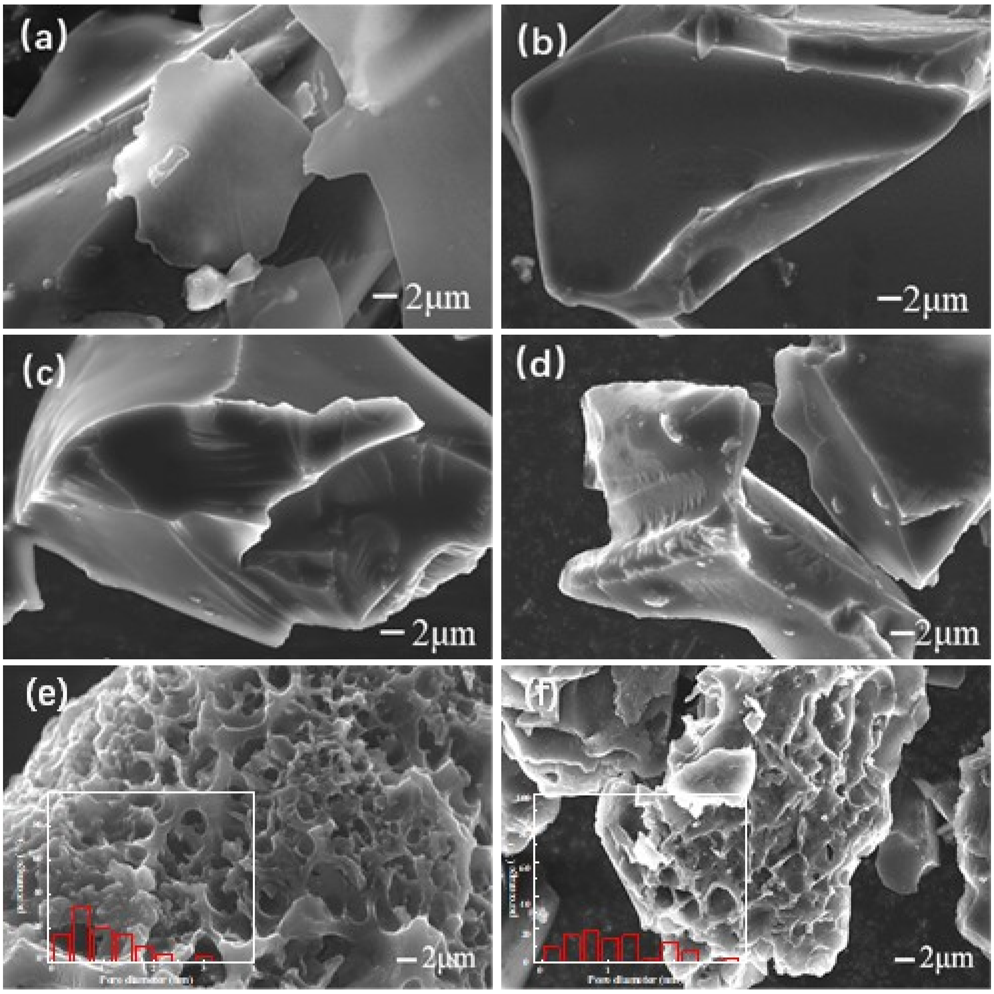

Fig. S1. SEM image of samples: BC_{800} (a); $BC_{2\text{-}800\text{-}0.5}$ (b); $BC_{2\text{-}800\text{-}1}$ (c); $BC_{2\text{-}800\text{-}2}$ (d); $BC_{2\text{-}800\text{-}4}$ (e); $BC_{2\text{-}800\text{-}6}$ (f).

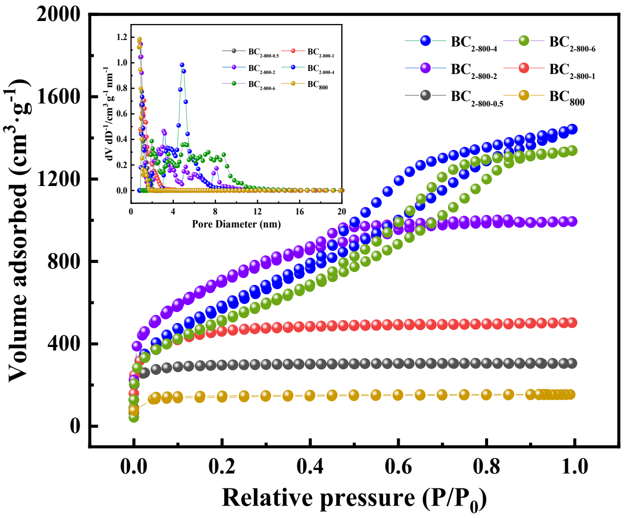

Fig. S2. N_2 adsorption-desorption isotherms and the pore-size distribution curves of BC_{800}, $BC_{2\text{-}800\text{-}0.5}$, $BC_{2\text{-}800\text{-}1}$, $BC_{2\text{-}800\text{-}2}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}800\text{-}6}$.

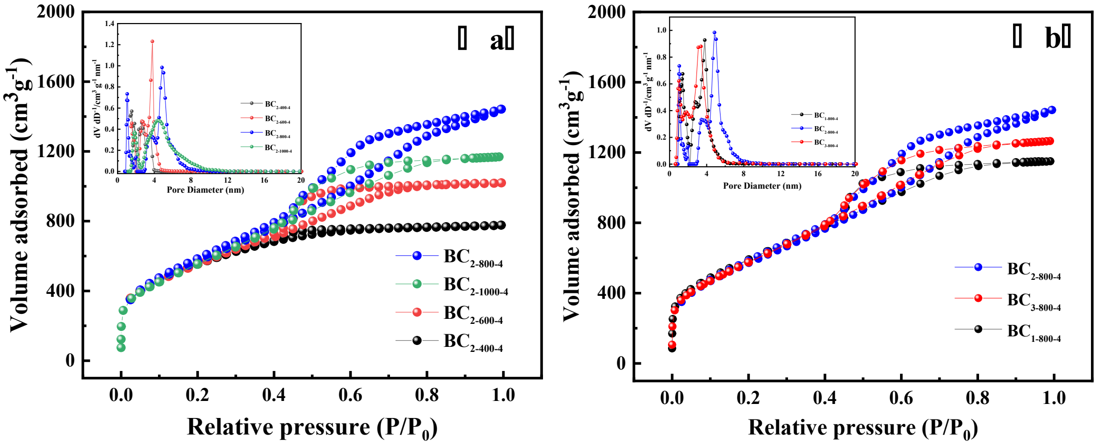

Fig. S3. N_2 adsorption-desorption isotherms and the pore-size distribution curves (a) of $BC_{2\text{-}400\text{-}4}$, $BC_{2\text{-}600\text{-}4}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}1000\text{-}4}$, N_2 adsorption-desorption isotherms and the pore-size distribution curves (b) of $BC_{1\text{-}800\text{-}4}$, $BC_{2\text{-}800\text{-}4}$, $BC_{3\text{-}800\text{-}4}$.

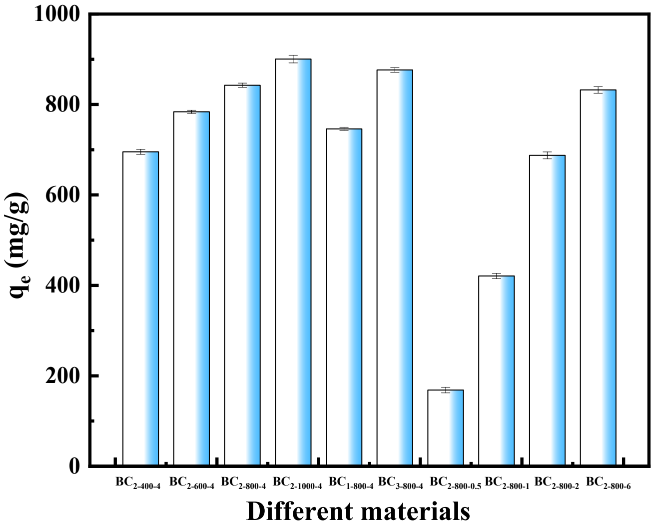

Fig. S4. Adsorption properties of $BC_{x\text{-}y\text{-}z}$

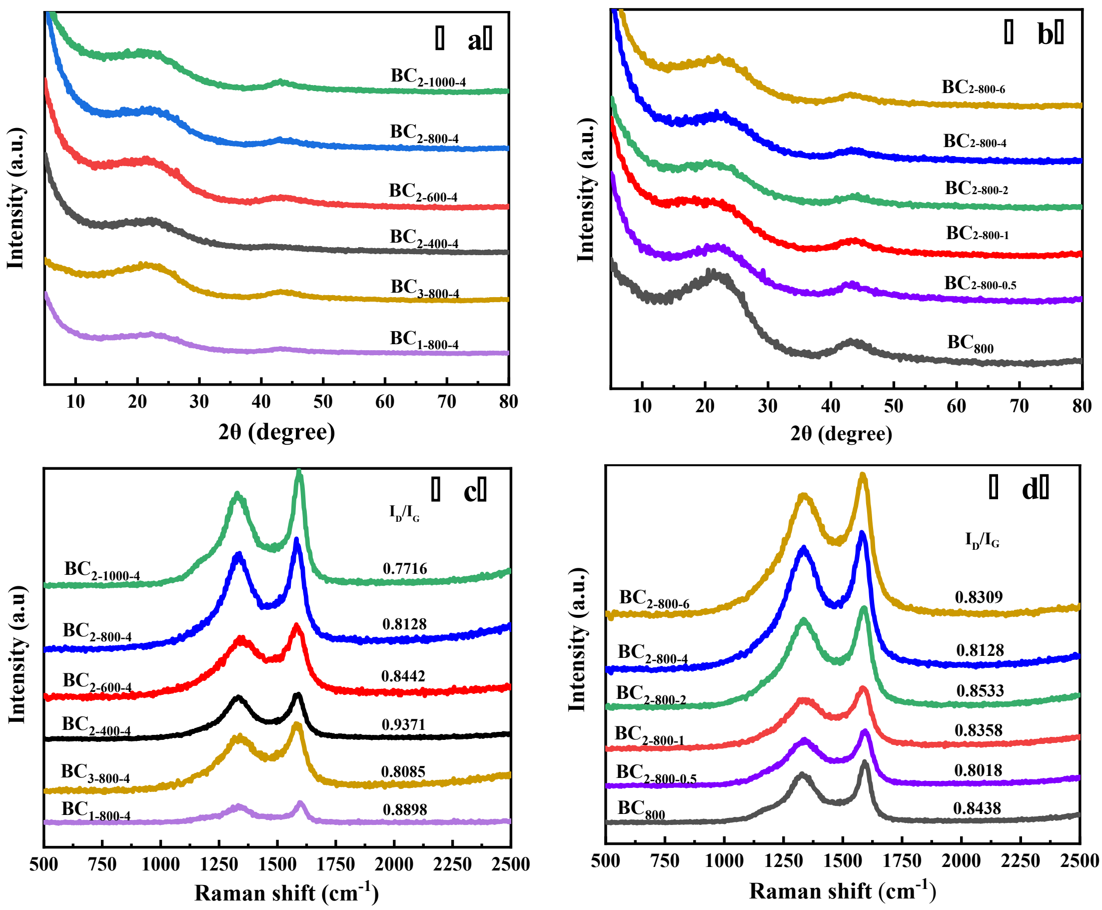

Fig. S5. (a) and (b) is the XRD patterns of $BC_{2\text{-}400\text{-}4}$, $BC_{2\text{-}600\text{-}4}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}1000\text{-}4}$, $BC_{1\text{-}800\text{-}4}$, $BC_{3\text{-}800\text{-}4}$, BC_{800}, $BC_{2\text{-}800\text{-}0.5}$, $BC_{2\text{-}800\text{-}1}$, $BC_{2\text{-}800\text{-}2}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}800\text{-}6}$. (c) and (d) is the Raman spectra of $BC_{2\text{-}400\text{-}4}$, $BC_{2\text{-}600\text{-}4}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}1000\text{-}4}$, $BC_{1\text{-}800\text{-}4}$, $BC_{3\text{-}800\text{-}4}$, BC_{800}, $BC_{2\text{-}800\text{-}0.5}$, $BC_{2\text{-}800\text{-}1}$, $BC_{2\text{-}800\text{-}2}$, $BC_{2\text{-}800\text{-}4}$, $BC_{2\text{-}800\text{-}6}$.

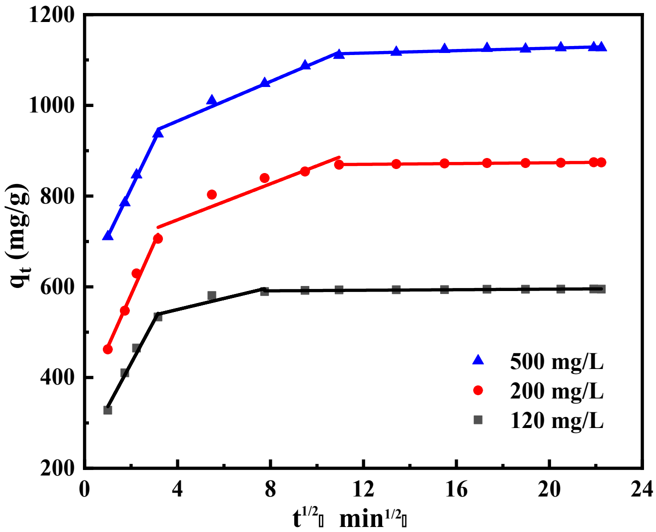

Fig. S6. Plots of the intra-particle diffusion model

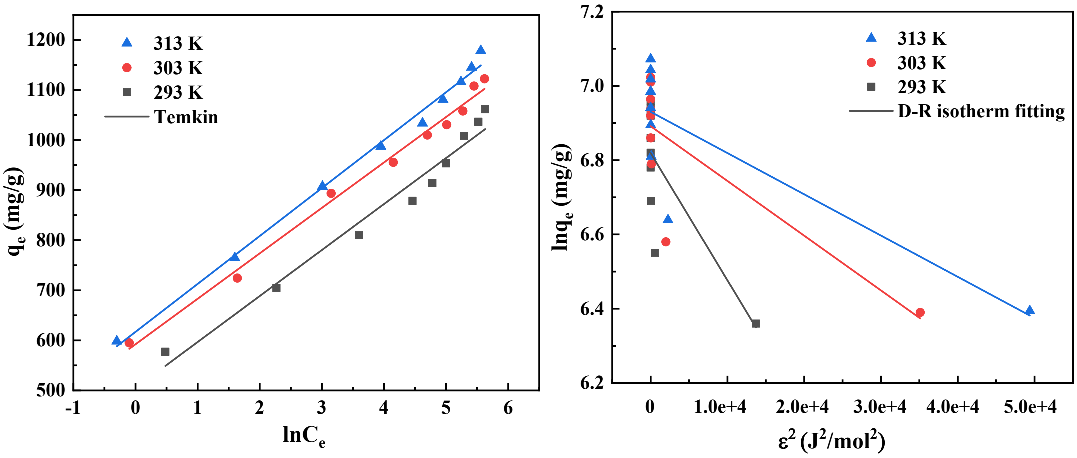

Fig. S7 (a) Temkin model and (b) Dubinin-Radushkevich model.

Table S1

Experimental conditions for adsorption of TC by $BC_{2-800-4}$

influencing factor	TC volume (mL)	C_0 (mg/L)	solution pH	reaction time (min)	temperature (K)
pH	10	200	2-11	240	303
kinetics	10	120、200、500	4	1-540	303
isotherms	10	120-500	4	240	293-313
thermodynamics	10	120-500	4	240	293-313
ionic strength	10	200	4	240	303
HA	10	200	4	240	303

(The concentration of inorganic ions is 0.9, 4.5, and 9 mmol/L, respectively, and HA concentrations are 5, 10, 15, and 20 mg/L, respectively.)

Table S2

Information of kinetics, isotherm, thermodynamic model and other related formulas in this study.

Type	Model	Equation	Parameter
Analytical methods	Adsorption capacity	$q_e = \frac{(C_0 - C_e)V}{m}$	q_e (mg/g) is the adsorption amount at equilibrium time; C_0 (mg/L) and C_e (mg/L) are the TC concentration in solution at initial and equilibrium time; V (L) is the solution volume; m (g) is the mass of the composite.
	Removal rate	$R\% = \frac{(C_0 - C_e)}{C_0} \times 100\%$	
Kinetics models	Pseudo-first-order	$Q_t = Q_e(1 - exp(-k_1 t))$	Q_t (mg/g) is the adsorption capacity at time t (min), Q_e (mg/g) is the adsorption capacity at equilibrium time, t is time (min), K_1 and K_2 are rates constant of pseudo-first order and pseudo-second order, respectively, a is the rate constant of chemisorption, b is constant of the surface coverage, K_{id} (mg/(g· min1/2)) is the rate constant of the intra-particle diffusion model, C (mg/g) is the constant of the intra-particle diffusion model
	Pseudo-second-order	$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}$	
	Elovich	$Q_t = \frac{1}{b} ln(1 + abt)$	
	Intra-particle diffusion	$Q_t = K_{id} t^{0.5} + C$	
Isotherm models	Langmuir	$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	Q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, and K_F and n are the Freundlich constant, respectively. a_T is the equilibrium bond constant concerned with the maximum energy of the bond, B and bT (J/mol) are the Temkin constant related to the sorption heat, R is the universal gas constant, and T is the Kelvin temperature. β is the activity coefficient related to the mean free energy of sorption (mol^2/J^2), and ε is the Polanyi potential.
	Freundlich	$Q_e = K_F C_e^{1/n}$	
	Temkin	$Q_e = B\ln K_T + B\ ln\ C_e$ $B = \frac{RT}{b_T}$	
	Dubinin-Radushkevich	$lnQ_e = lnQ_d - \beta\varepsilon^2$ $\varepsilon = RTln(1 + \frac{1}{C_e})$	
Thermodynamics	Gibbs-Helmholtz equation	$lnK_C = -\frac{\triangle H^0}{RT} + \frac{\triangle S^0}{R}$ $\triangle G^0 = \triangle H^0 - T \triangle S^0$ $K_C = \frac{Q_e}{C_e}$	K_c (L/mg) is thermodynamic equilibrium constant, ΔS° (J/mol· K) is entropy change，ΔH° (KJ/mol) is enthalpy change, ΔG° (KJ/mol) is gibbs free energy.

Table S3

Porosity characteristic of different adsorbents

Samples	BET Surface Area (m^2/g)	Total Pore Volume(cm^3/g)	Fractions of Micropores (%)	Average Pore Diameter (nm)
BC_{800}	372	0.21	100	1.01
$BC_{2-800-0.5}$	870	0.42	41	1.03
$BC_{2-800-1}$	1176	0.69	51	1.23
$BC_{2-800-2}$	1521	1.42	50	1.17
$BC_{2-800-4}$	1645	1.72	14	4.37
$BC_{2-800-6}$	1609	1.97	8	3.68
$BC_{1-800-4}$	1331	1.64	27	3.79
$BC_{2-800-4}$	1645	1.72	14	4.37
$BC_{3-800-4}$	1711	1.86	12	4.84
$BC_{2-400-4}$	1342	1.09	52	1.54
$BC_{2-600-4}$	1407	1.48	31	3.79
$BC_{2-800-4}$	1645	1.72	14	4.37
$BC_{2-1000-4}$	1707	1.73	9	4.84

Table S4

Kinetic parameters for TC adsorption on $BC_{2\text{-}800\text{-}4}$ in different initial concentrations.

Kinetic model and paranmeters	C_0 (mg/L)		
	120	200	500
$q_{e.exp}$ (mg/g)	594.50	874.70	1127.00
Pseudo-first-order- dynamics model			
$q_{e.cal}$ (mg/g)	588.20	838.50	1090.00
K_1 g/(mg·min)	0.4773	0.2818	0.3576
R^2	0.8554	0.8525	0.7645
Pseudo-second-order- dynamics model			
$q_{e.cal}$(mg/g)	596.50	866.30	1111.50
K_2 g/(mg·min)	1.50×10^{-3}	0.62×10^{-3}	0.57×10^{-3}
R^2	0.9694	0.9668	0.9719
Elovich			
a	1.23×10^{6}	3.01×10^{6}	2.28×10^{6}
b	0.0260	0.0190	0.0140
R^2	0.7959	0.8668	0.9107
Intraparticle diffusion model			
K_{i1} mg/(g $min^{1/2}$)	87.43	104.30	105.50
C_1	240.90	352.80	605.50
R_1^2	0.9872	0.9836	0.9985
K_{i2} mg/(g $min^{1/2}$)	7.4360	15.7700	20.1600
C_2	530.90	725.70	946.70
R_2^2	0.8663	0.8888	0.9836
K_{i3} mg/(g $min^{1/2}$)	0.2527	0.4029	1.1060
C_3	588.70	864.70	1099.10
R_3^2	0.8127	0.9709	0.8393

Table S5

Isotherm parameters for TC adsorption on $BC_{2\text{-}800\text{-}4}$

Models and parameters	293 K	303 K	313 K
Langmuir			
q_m (mg/g)	954.81	1026.20	1061.90
K_L (L/mg)	0.4237	0.7066	0.7833
R^2	0.7048	0.7679	0.7443
Freundlich			
K_F ($mg^{1-n}L^n$/g)	532.39	613.62	628.98
$1/n_F$	0.1244	0.1109	0.1136
R^2	0.9881	0.9915	0.9964
Temkin			
K_T (L/g)	242.25	544.57	550.04
b_T (J/mol)	26.53	27.76	27.19
R^2	0.9653	0.9903	0.9926
Dubinin–Radushkevich			
Q_d (mg/g)	915.06	983.38	1022.49
β (mol^2/J^2)	3.42×10^{-3}	1.47×10^{-3}	1.10×10^{-3}
R^2	0.6054	0.6436	0.6707

Table S6

Comparison of the equilibrium adsorption of the $BC_{2\text{-}800\text{-}4}$ with other Biochar adsorbents for TC removal.

Adsorbents	activator	Adsorbates	q_{max}(mg/g)	BET Surface Area (m^2/g)	Activation Temperature (°C)	References
$NCES_{800\text{-}1\text{-}0.5}$	$NaHCO_3$	tetracycline	154.45	379	800	[1]
HSBB600	-	tetracycline	94.69	319	600	[2]
Fe-BCK0.5-VB6	KOH	tetracycline	70.80	455	700	[3]
MSBC	NaOH	tetracycline	98.33	165	300	[4]
$ACS_{300\text{-}1}$	H_3PO_4	tetracycline	227.30	464	300	[5]
activated BC	NaOH	tetracycline	274.80	960	500	[6]
SABC-700	-	tetracycline	412.95	171	700	[7]
GSP-BC	KOH	tetracycline	1911.80	3686	800	[8]
Zn-BC	$ZnCl_2$	tetracycline	93.44	852	700	[9]
ZBAB	$ZnCl_2$	ciprofloxacin	250.00	1223	700	[10]
activated BC	$ZnCl_2$	Malachite green dye	90.10	51	800	[11]
ZnVB1–1	$ZnCl_2$	Cr (VI)	236.81	940	700	[12]
Zn2PT350-700	$ZnCl_2$	methylene blue	590.20	877	700	[13]
$BC_{2\text{-}800\text{-}4}$	$ZnCl_2$	tetracycline	1122.20	1645	800	Present work

Table S7

Adsorption thermodynamic parameters for TC adsorption on $BC_{2\text{-}800\text{-}4}$

	Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
TC	293	-14.31	30.95	154.94
	303	-16.33		
	313	-17.42		

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