Supplementary Information

Rapid and efficient removal of multiple aqueous pesticides by one-step construction boric acid modified biochar

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1. Adsorption capacity calculation equation

The equilibrium adsorption(q_e) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)\,V}{m}$$

Where C_0 (initial) and C_e (equilibrium) denote pesticide concentrations (mg L^{-1}), V is the solution volume(L), and *m* is the mass of sorbent (g).

2. Kinetics model

The pseudo-first-order (Eq. (S1)), pseudo-second-order model (Eq. (S2)), Elovich model (Eq. (S3)), and Intra-particle diffusion model (Eq. (S4)) were used to describe the sorption kinetic data. The equations of the four kinetic models are represented as follows:

Pseudo-first-order model:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{S1}$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(S2)

Elovic model:

$$q_t = \beta \ln\,(a\beta) + (\ln t) \tag{S3}$$

Intra-particle diffusion model:

$$q_t = K_p\sqrt{t} + C \tag{S4}$$

The symbols in the formula are explained as follows:

q_t represents the adsorption capacity at time t (min), (mg g^{-1}); q_e represents the adsorption capacity at the equilibrium time (mg g^{-1}); t denotes the contact time (min); K_1 denotes the pseudo-first-order rate constant (min^{-1}); K_2 denotes the pseudo-second-order rate constant (g mg^{-1} min^{-1}). α is the sorption kinetic at the beginning (mg g^{-1} min^{-1}) and β is the sorption constant related to the extent of surface coverage and the activation energy for chemisorption during the experiments (g mg^{-1}). The constants α and β can be obtained from the slope and intercept of the linear plot of q_t Vs lnt.

K_p denotes the intra-particle diffusion rate constant (mg g^{-1} $min^{0.5}$); C denotes the constant about the thickness of the boundary layer.

3. Isotherms models

Langmuir (Eq. (S5)), Freundlich (Eq. (S6)), and Temkin models (Eq. (S7)) were applied to determine the sorption characteristics. The three isotherm equations are provided as follows:

Langmuir model:

$$\frac{1}{q_e} = \frac{1}{k_L q_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{S5}$$

Freundlich model:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{S6}$$

Temkin model:

$$q_e = B \ln C_e + B \ln K_T \tag{S7}$$

The symbols in the formula are explained as follows:

q_e denotes the adsorption capacity at the equilibrium time (mg g^{-1}); q_m denotes the maximum adsorption capacity (mg g^{-1}). K_L denotes the Langmuir constant (L mg^{-1}); C_e denotes the equilibrium concentration of pesticides after adsorption (mg L^{-1}); K_F denotes the Freundlich constant (L mg^{-1}). B is a constant related to the heat of sorption and it is defined by the expression B= RT/b, b is the Temkin constant (J mol^{-1}), T is the absolute temperature (K), R is the gas constant (8.314 J mol^{-1} K), and A is the Temkin isotherm constant (L g^{-1}). From the plot of q_e Vs lnC_e, B and A can be calculated from the slopes (B) and intercepts (BlnA) respectively.

Table S1. Multiple reaction monitoring (MRM) data acquisition parameters of HPLC-MS/MS for the four pesticides.

Pesticides	precursor ion（m/z）	product ion	Fragmentor (V)	Collision Energy（V）
Tricyclazole	190	135.9*	130	28
		163		20
Propiconazole	342.0	159*	90	30
		69		20
Imidacloprid	256	209.1*	73	10
		175.1		15
Thiamethoxam	292	211*	85	5
		132.1		20

*Quantitative ion

Table S2. Elemental composition of different biochars

Sample	C, wt%	H, wt%	O, wt%	B, wt%	N, wt%	H/C	O/C	(N+O)/C
WA	82.88	1.924	10.908	0.0854	0.69	0.0232	0.1316	0.0315
WAB0.5	74.18	2.627	18.797	0.045	0.85	0.0354	0.2534	0.0469
WAB1	71.47	2.467	21.719	0.1017	1.06	0.0345	0.3039	0.0493
WAB2	69.23	2.478	26.083	0.228	1.15	0.0358	0.3768	0.0524
WAB4	69.78	2.489	26.591	0.199	1.21	0.0357	0.3811	0.0530

Table S3. The XPS results of WA (pristine biochar) and WAB4 on C and O atomic percentages and distributions.

Sample	C (%)	O (%)	C/O	C1s (%)			O1s (%)		
				C=C	C-O	O-C=O	C=O	-OH	CO/CO_2
WA	87.63	10.91	8.03	72.39	18.97	8.64	49.99	50.01	-

WAB4	80.32	18.79	4.27	74.17	13.17	12.66		56.64	38.29	5.07

Table S4. Key physicochemical properties of investigated pesticides.

pesticides	Water Solubility ($mg\ L^{-1}$) 20℃	Lipophilicity (log P)	Soil Affinity (log K_{oc})	pK_a	H-bonding acceptor parameter	H-bonding donor parameter
Tricyclazole	596	1.4	169	ND[a]	3	0
Imidacloprid	610	0.57	-	ND	4	1
Thiamethoxam	4100	-0.13	56.2	ND	6	0
Propiconazole	150	3.72	1086	1.09	3	1

[a] No dissociation.

Table S5. Thermodynamic parameters of four pesticides adsorption on WAB4

Pesticides	T	K_0	ΔG ($KJ\ mol^{-1}$)	ΔH ($KJ\ mol^{-1}$)	ΔS ($J\ mol^{-1}\ K^{-1}$)
Tricyclazole	298	6.33	-4.572	9.0879	45.7270
	308	6.83	-4.920		
	318	7.98	-5.491		
Propiconazole	298	6.46	-4.622	0.8495	18.2908
	308	6.57	-4.821		
	318	6.6	-4.989		
Imidacloprid	298	5.80	-4.355	0.4009	15.9454
	308	5.80	-4.501		
	318	5.86	-4.647		
Thiamethoxam	298	5.36	-4.514	-6.0337	-6.2560
	308	5.01	-4.129		
	318	4.60	-4.033		

Table S6 Physical and chemical properties of real water samples

Physico-chemical indicators	Deionized water	Tap water	Paddy water	River water
pH	7.06	7.07	7.04	8.2
Hardness	4	202.18	154.13	126.11
Alkalinity	8.5	166	126	138
CO_3^{2-}	0	0	0	4.5
HCO_3^-	2.745	21.655	17.995	5.49
Ca^{2+}	0.5418	47.490	39.890	18.736
K^+	0.0159	1.6918	1.7671	13.675
Mg^{2+}	0.1842	21.316	13.559	13.219
Na^+	0.6355	18.794	15.209	87.203
Cl^-	8.5118	13.0414	15.8832	60.4238

NO_3^-	39.8307	57.0348	46.0599	58.1675
SO_4^{2-}	7.9565	28.9050	15.4988	49.9895

Table S7. *Daphnia. magna* immobilization and mortality for different concentrations of WAB4

Concentration of WAB4 (mg L^{-1})	Immobilization		Mortality	
	24 h	48 h	24 h	48 h
0	0	0	0	0
1	0	0	0	0
10	0	0	0	0
50	0	0	0	0
100	0	0	0	0
200	0	0	0	0

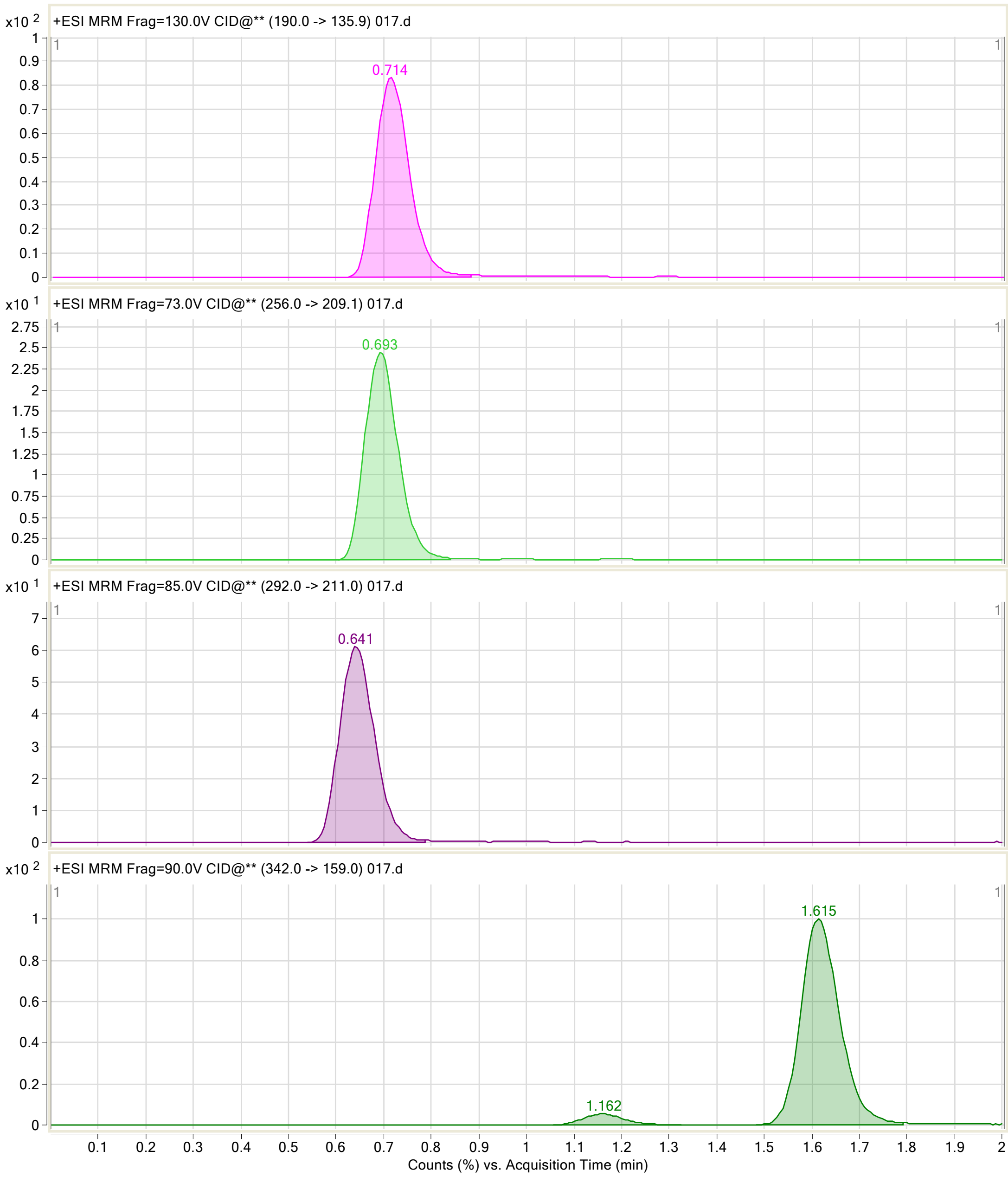

Fig. S1. LC-MS/MS spectrograms of five pesticides

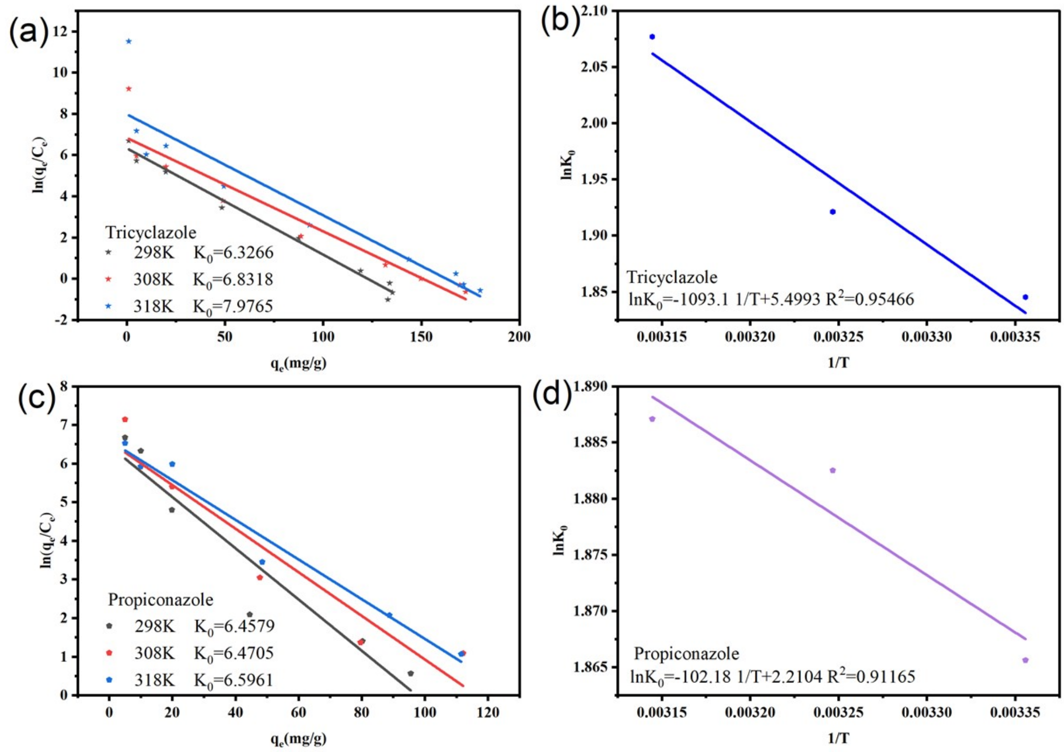

Fig. S2. (a), (b) van't Hoff plots of tricyclazole adsorption onto WAB4; (c), (d) van't Hoff plots of propiconazole adsorption onto WAB4

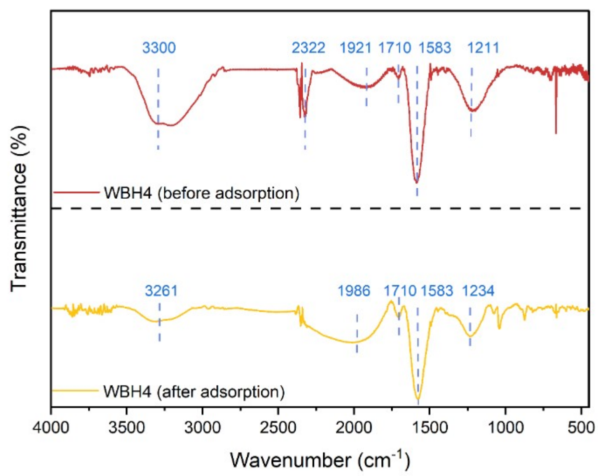

Fig. S3. FTIR spectrum of WAB4 before and after adsorption of four pesticides

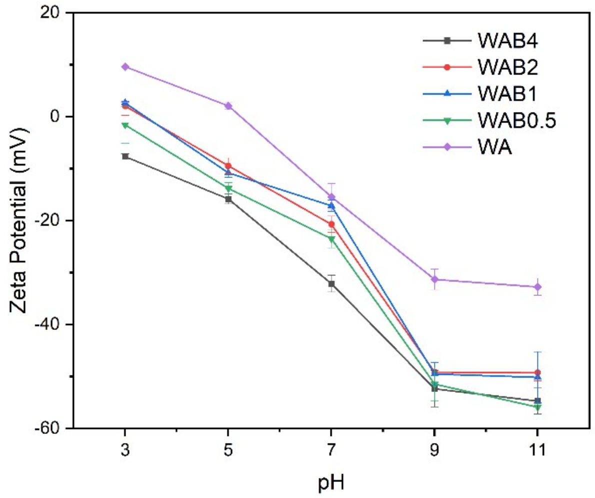

Fig. S4. The Zeta potential of all materials at varying solution pH from 3 to 11 (adsorbent dosage=1 g L^{-1}).