Electronic Supplementary Material (ESI) for RSC Advances.

Figure Captions

Fig. S1. Particle size distribution of BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Fig. S2. TG and DTG profiles of BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Fig.S3. SEM micrographs of (a) and (d) BHP-char, (b) and (e) NH_4Cl-BHP-char, and (c) and (f) NH_4Cl-BHP-char/Fe_3O_4.

Fig.S4. FTIR spectra of NH_4Cl-BHP/Fe_3O_4 before and after co-adsorption of Zn^{2+} and TC.

Table Captions

Table S1. Structure and properties of TC.

Table S2. Particle size distribution of BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Table S3. Parameters of pseudo-first-order and pseudo-second-order models for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Table S4. Parameters of isotherms for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4. Conditions: pH of single-component adsorption of TC was 4.0, pH of single-component adsorption of Zn(II) was 6.5, pH of co-adsorption of TC/Zn(II) was 6.0, adsorbent concentrations 0.5 g L^{-1}, temperature 25 ℃, contact time 120 min.

Table S5. Parameters of thermodynamic for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4. Conditions: pH of single-component adsorption of TC was 4.0, pH of single-component adsorption of Zn(II) was 6.5, pH of co-adsorption of TC/Zn(II) was 6.0, adsorbent concentrations 0.5 g L^{-1}, initial TC/Zn(II) concentrations 25 mg L^{-1}, contact time 120 min.

Table S6. Constants of film diffusion model for TC and Zn(II) on BHP and NH_4Cl-BHP-char/Fe_3O_4.

Table S7. Constants of Intra-particle diffusion model for TC and Zn(II) on BHP and NH_4Cl-BHP-char/Fe_3O_4.

Table S1. Structure and properties of TC.

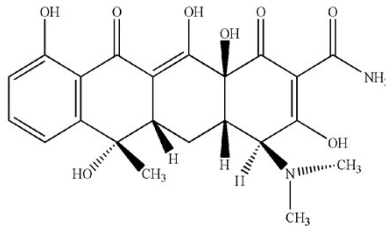
Compound	Chemical formula	Molecular weight	Density (g cm^{-3})	Refractive index	Melting point (℃)	flash point (℃)	Molecular structure
Tetracycline	$C_{22}H_{24}N_2O_8$	444.43	1.644	1.650	172-174	431.9	

Table S2. Particle size distribution of BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Adsorbent	D10[a] (μm)	D50[b] (μm)	D90[c] (μm)
BHP-char	34.73	101.1	211.3
NH_4Cl-BHP-char/Fe_3O_4	0.969	3.889	8.984

[a] Particle diameter corresponding to 10% cumulative (from 0 to 100%) undersize particle size distribution;

[b] Particle diameter corresponding to 50% cumulative (from 0 to 100%) undersize particle size distribution;

[c] Particle diameter corresponding to 90% cumulative (from 0 to 100%) undersize particle size distribution.

Table S3. Parameters of pseudo-first-order and pseudo-second-order models for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Single-component adsorption	Adsorbent	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
			k_1 (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})
TC	BHP-char	28.80	0.0328	0.9759	21.53	0.0050	0.9929	28.99
	NH_4Cl-BHP-char/Fe_3O_4	47.55	0.0307	0.9921	38.02	0.0022	0.9959	48.78
Zn^{2+}	BHP-char	38.26	0.0734	0.9798	25.33	0.0074	0.9977	39.53
	NH_4Cl-BHP-char/Fe_3O_4	49.23	0.0691	0.9791	28.51	0.0094	0.9931	48.08
Co-adsorption	Adsorbent	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
			k_1 (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})
TC	BHP-char	36.16	0.0799	0.9852	28.59	0.0064	0.9919	37.88
	NH_4Cl-BHP-char/Fe_3O_4	48.55	0.0871	0.9798	29.67	0.0057	0.9990	51.55
Zn^{2+}	BHP-char	39.51	0.0928	0.9806	18.48	0.0226	0.9970	39.06
	NH_4Cl-BHP-char/Fe_3O_4	49.66	0.0965	0.9934	29.92	0.0109	0.9959	50.25

Table S4. Parameters of isotherms for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Single-component adsorption	Adsorbent	Langmuir			Freundlich		
		q_L (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	n	R^2
TC	BHP-char	39.68	0.3007	0.9913	6.68	1.7265	0.9746
	NH_4Cl-BHP-char/Fe_3O_4	106.38	0.8174	0.9951	35.59	1.3841	0.9777
Zn^{2+}	BHP-char	109.89	0.1033	0.9966	8.06	1.3972	0.9771
	NH_4Cl-BHP-char/Fe_3O_4	151.52	0.4342	0.9977	27.04	1.5230	0.9540

Single-component adsorption	Adsorbent	Temkin			D-R		
		K_T (L g^{-1})	β_T (kJ mol^{-1})	R^2	q_D (mg g^{-1})	E (kJ mol^{-1})	R^2
TC	BHP-char	10.03	0.4385	0.9169	16.92	2.9090	0.8413
	NH_4Cl-BHP-char/Fe_3O_4	38.47	0.1839	0.8710	41.16	3.9724	0.9148
Zn^{2+}	BHP-char	5.03	0.1670	0.9032	35.38	2.2854	0.7770
	NH_4Cl-BHP-char/Fe_3O_4	24.48	0.1266	0.9197	64.94	3.4598	0.8874

Co-adsorption	Adsorbent	Langmuir			Freundlich		
		q_L (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	n	R^2
TC	BHP-char	76.92	0.1783	0.8938	9.38	1.5202	0.9989
	NH_4Cl-BHP-char/Fe_3O_4	126.58	1.1791	0.9448	61.14	1.3307	0.9948
Zn^{2+}	BHP-char	192.31	0.081	0.7871	12.62	1.347	0.9986
	NH_4Cl-BHP-char/Fe_3O_4	357.14	1.077	0.8957	216.35	1.157	0.9943

Co-adsorption	Adsorbent	Temkin			D-R		
		K_T (L g^{-1})	β_T (kJ mol^{-1})	R^2	q_D (mg g^{-1})	E (kJ mol^{-1})	R^2
TC	BHP-char	10.68	0.2858	0.7772	19.17	5.9133	0.7445
	NH_4Cl-BHP-char/Fe_3O_4	70.99	0.1745	0.8038	45.92	4.703	0.9231
Zn^{2+}	BHP-char	7.99	0.1288	0.7459	38.83	3.902	0.7035
	NH_4Cl-BHP-char/Fe_3O_4	128.59	0.08468	0.7880	108.20	3.841	0.9341

Table S5. Parameters of thermodynamic for the adsorption of TC and Zn(II) on BHP-char and NH_4Cl-BHP-char/Fe_3O_4.

Single-component adsorption	Adsorbent	ΔG^o (KJ mol^{-1})					ΔH^o (KJ mol^{-1})	ΔS^o (KJ mol^{-1})	R^2
		293K	298K	303K	308K	313K			
TC	BHP-char	-1.346	-2.588	-3.830	-5.072	-6.314	71.472	0.2484	0.9939
	NH_4Cl-BHP-char/Fe_3O_4	-6.519	-8.773	-11.027	-13.281	-15.535	125.633	0.4508	0.9902
Zn^{2+}	BHP-char	-2.948	-4.748	-6.548	8.348	-10.148	102.586	0.3600	0.9991
	NH_4Cl-BHP-char/Fe_3O_4	-10.049	-12.075	-14.100	-16.126	-18.151	108.706	0.4051	0.9936

Co-adsorption	Adsorbent	ΔG^o (KJ mol^{-1})					ΔH^o (KJ mol^{-1})	ΔS^o (KJ mol^{-1})	R^2
		293K	298K	303K	308K	313K			
TC	BHP-char	-2.344	-4.199	-6.055	-7.910	-9.766	106.444	0.3711	0.9986
	NH_4Cl-BHP-char/Fe_3O_4	-8.167	-10.301	-12.434	-14.568	-16.701	116.920	0.4267	0.9989
Zn^{2+}	BHP-char	-3.209	-5.191	-7.173	-9.155	-11.137	112.996	0.3964	0.9947
	NH_4Cl-BHP-char/Fe_3O_4	-12.299	-13.858	-15.417	-16.976	-18.535	79.105	0.3118	0.9961

Table S6. Constants of film diffusion model for TC and Zn(II) on BHP and NH_4Cl-BHP-char/Fe_3O_4.

Adsorbate	Adsorbent	Film diffusion model		
		k_F (min^{-1})	A	R^2
TC (Single-component adsorption)	BHP-char	0.0328	-0.2908	0.9725
	NH_4Cl-BHP-char/Fe_3O_4	0.0298	-0.1342	0.9824
Zn^{2+} (Single-component adsorption)	BHP-char	0.0734	-0.4123	0.9769
	NH_4Cl-BHP-char/Fe_3O_4	0.0691	-0.5462	0.9761
TC (Co-adsorption)	BHP-char	0.0779	-0.2350	0.9831
	NH_4Cl-BHP-char/Fe_3O_4	0.0644	-0.0257	0.9692
Zn^{2+} (Co-adsorption)	BHP-char	0.0928	-0.7599	0.9778
	NH_4Cl-BHP-char/Fe_3O_4	0.0965	-0.5068	0.9925

Table S7. Constants of Intra-particle diffusion model for TC and Zn(II) on BHP and NH_4Cl-BHP-char/Fe_3O_4.

Adsorbate	Adsorbent	Intra-particle diffusion model					
		k_{s1} (mg g min^{-1})	C_1 (mg g^{-1})	R^2	k_{s2} (mg g min^{-1})	C_2 (mg g^{-1})	R^2
TC (Single-component adsorption)	BHP-char	4.743	0.209	0.9971	1.388	14.514	0.9998
	NH_4Cl-BHP-char/Fe_3O_4	8.977	-5.610	0.9566	3.745	9.867	0.9987
Zn^{2+} (Single-component adsorption)	BHP-char	8.768	1.919	0.9785	2.141	23.114	0.9525
	NH_4Cl-BHP-char/Fe_3O_4	7.959	12.063	0.9960	3.080	28.392	0.9604
TC (Co-adsorption)	BHP-char	7.678	0.042	0.9977	1.844	22.965	0.9301
	NH_4Cl-BHP-char/Fe_3O_4	8.519	-2.061	0.9815	5.656	7.927	0.9724
Zn^{2+} (Co-adsorption)	BHP-char	5.802	15.536	0.9796	1.558	29.681	0.9407
	NH_4Cl-BHP-char/Fe_3O_4	7.892	13.812	0.9846	4.288	24.733	0.9670

Text 1

Dertermination of Zn(II)

FAAS determination conditions: Wavelength of 213.86 nm, hollow cathode lamp current of 15 mA, slit of 2.7/1.8 mm, airflow rate of 10 L min^{-1}, and acetylene flow rate of 2.5 L min^{-1}.

Preparation of 50 mg L^{-1} standard solution of Zn(II): Transfer 5 mL of 1,000 mg L^{-1} stock solutions of Zn(II) to a 100 mL volumetric flask, and dilute with ultrapure water to a specific volume.

Preparation of Zn(II) working standard solution: Transfer 0, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mL of 50 mg L^{-1} standard solution of Zn(II) to a 50 mL volumetric flask, respectively, and dilute with 1% nitric acid to volume. Zn(II) working standard solution concentrations were 0, 1.0, 2.0, 4.0, 6.0. 8.0 and 10.0 mg L^{-1}, respectively.

The linear relationship between absorbance and concentration is

$$y = 0.0567x + 0.438 \qquad (R^2=0.9995)$$

Determination of TC

Preparation of TC working standard solution: Transfer 0, 0.05, 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 mL of 1,000 mg L^{-1} stock solutions of TC to a 100 mL volumetric flask, respectively, and dilute with ultrapure water to a specific volume. TC working standard solution concentrations were 0, 0.5, 1.0, 2.5, 5.0, 10.0, 15.0 and 20.0 mg L^{-1}, respectively.

The linear relationship between absorbance and concentration is

$$y = 0.0354x + 0.2814 \qquad (R^2=0.9992)$$

Text 2

Pseudo-first order model $\ln(q_e - q_t)=\ln q_e - k_1 t$

Pseudo-second order model $\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e}$

Film diffusion model $\ln(1-\frac{q_t}{q_e})=-k_F t+A$

Intra-particle diffusion model $q_t=k_S t^{1/2}+I$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of TC or Zn(II) adsorbed on the biochar at equilibrium and at time t (min), respectively, k_1 (1 min^{-1}) is the rate constant of pseudo-first order adsorption. k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order adsorption. k_F (1 min^{-1}) and A are liquid film diffusion constants, where k_S (mg g^{-1} $min^{-0.5}$) is the rate constant of intra-particle diffusion model, and I (mg g^{-1}) is a constant describing the thickness of boundary layer.

Text 3

Langmuir isotherm $$\frac{C_e}{q_e}=\frac{1}{q_L K_L}+\frac{C_e}{q_L}$$

Freundlich isotherm $$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e$$

Temkin isotherm $$q_e=\frac{RT}{\beta_T}\ln(K_T C_e)$$

D-R isotherm $$\ln q_e=\ln q_D-(\frac{RT}{\sqrt{2E}})^2\times(\ln(1+\frac{1}{C_e}))^2$$

where q_L (mg g^{-1}) is the Langmuir maximum adsorption capacity of TC or Zn(II), K_L (L mg^{-1}) is the Langmuir constant termed as apparent energy of adsorption, K_F ((mg g^{-1}) (L $mg^{-1})^{1/n}$) is the Freundlich constants related to adsorption capacity, n is a measure of adsorption linearity, β_T (J mol^{-1}) is the Temkin constant related to heat of adsorption, K_T (L g^{-1}) is the Temkin isotherm constant, R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature, q_D (mg g^{-1}) is the D-R maximum adsorption capacity of TC or Zn(II), and E (J mol^{-1}) is mean free energy of adsorption per molecule of the adsorbate.

Text 4

$$K_C=q_e/C_e$$

$$\Delta G^o=-RT\ln K_C$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

where K_C (ml g^{-1}) is the thermodynamic equilibrium constant.