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Electronic Supplementary Information

Green synthesis of ZnO coated Hybrid Biochar for the synchronous removal of Ciprofloxacin and Tetracycline in Water

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1. Materials preparation

1.1. Purification of clay

The clay was suspended in distilled water for several hours. After this, the mixture was stirred in hydrogen peroxide solution until effervescence ceased in order to remove organics present in the clay. The mixture was left to stand for 12 hours after which it was filtered. The clay was washed with distilled water to remove any hydrogen peroxide remaining and oven dried at 343K.

2. Van't Hoff Equation

$$lnln\, Kd = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^0}{RT}\right) \quad (1)$$

$$\Delta G^o = -RTlnK_d \quad (2)$$

K_d is the equilibrium distribution coefficient, which is the ratio of the amount adsorbed on the adsorbents (mg/g) to the equilibrium concentration in solution (mg/L); T is the solution temperature (K) and R is the gas constant (8.314 $J.K^{-1}.mol^{-1}$).

Table S1: Adsorption isotherm model parameters for the adsorption of CIP and TET onto KCB, KCB-A and KCB-B

Model	Equation	Parameter		CIP			TET		
				KCB	KCB-A	KCB-B	KCB	KCB-A	KCB-B
Freundlich	$qe = K_F.Ce^{1/n}$	K_F(mg.g^{-1}	(L.mg^{-1})$^{1/nF}$	12.63	10.22	8.05	7.02	4.78	3.73
		nF		2.03	1.48	1.35	1.73	1.63	1.22
		R^2		0.948	0.996	0.984	0.911	0.946	0.927
Langmuir	$qe = \frac{q_{max}.K_L.Ce}{1 + K_L.Ce}$	q_{max} (mg/g)		71.10	139.92	228.73	118.01	116.55	231.93
		K_L (L.mg^{-1})		0.22	0.06	0.02	0.035	0.021	0.013
		R_L		0.05	0.17	0.34	0.26	0.37	0.40
		R^2		0.977	0.999	0.985	0.949	0.965	0.938
Dubinin-Radushkevich	$qe = q_m EXP(-\beta$	q_m (mol.g^{-1})		20.70	72.20	73.37	81.35	66.64	80.41
		β (mol^2.KJ^{-2})		9.7x10^{-3}	1.0x10^{-4}	2.9x10^{-3}	0.04	0.02	0.03
		E		7.15	69.11	13.06	3.52	4.93	4.17
		R^2		0.674	0.960	0.9722	0.974	0.929	0.971
Temkin	$qe = \frac{RT}{b_T} lnln(K_T.$	b_T (J.mol^{-1})		166.72	118.78	145.01	96.78	145.01	92.84
		K_T(L.mg^{-1})		2.34	1.74	2.61	0.36	0.31	0.34
		B		15.11	21.21	17.37	26.03	22.05	27.13
		R^2		0.989	0.988	0.948	0.970	0.962	0.878
Brouers-Sotolongo	$qe = q_{BS}(1 - exp($	q_{bs} (mg/g)		59.11	101.59	81.77	84.28	80.07	89.36
		K_{BS} (L/mg)		0.207	0.08	0.0004	0.003	0.02	9.8x10^{-4}
		α_{BS}		1.34	0.95	3.02	2.14	1.15	
		R^2		0.989	0.999	0.991	0.997	0.969	2.50
									0.990
Langmuir-Freundlich	$qe = \frac{Q^0(KCe)^n}{1 + (KCe)^n}$	Q^o		60.61	137.65	84.70	85.39	89.17	90.25
		K		0.40	0.06	0.09	0.08	0.04	0.08

	nL-F	1.59	1.01	04.64	2.62	1.38	3.23
	R^2	0.990	0.999	0.984	0.995	0.941	0.992

qe is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q_{max} is the maximum monolayer adsorption capacity (mg/g),K_L is the constant related to the affinity of the adsorbate to the sorbent, A_T is the temkin equilibrium binding constant (L/mg) corresponding to maximum binding energy and B is the isotherm constant related to the heat of adsorption (J/mol), b is a constant, R is gas constant (8.314 J/mol/K) and T is temperature (K), q_{BS} is the saturation capacity in mg/g; K_{BS} is K_F/q_{BS} where K_F is the Freundlich constant; α_{BS} is a measure of the width of the sorption energy distribution, K_F is an empirical constant indicative of the relative adsorption capacity of the adsorbent and 1/n is an adsorption constant that shows the intensity of heterogeneity of adsorption.

Table S2: Kinetics model parameters for the adsorption of CIP and TET onto KCB, KCB-A and KCB-B

Model	Equation	Parameter	CIP			TET		
			KCB	KCB-A	KCB-B	KCB	KCB-A	KCB-B
Pseudo first-order	$qt = qe - exp(lnqe - K$	qe (mg/g)	7.55	7.29	7.66	7.32	7.33	7.18
		$k_1(min^{-1})$	0.31	1.20	0.60	1.46	0.59	1.67
		RMSE	1.49	0.78	0.25	0.14	0.20	0.28
Pseudo second-order	$qt = \frac{qe^2 K_2 t}{qeK_2 t + 1}$	qe (mg/g)	8.07	7.62	8.03	7.40	7.72	7.27
		k_2(g/mg.min)	0.07	0.28	0.15	0.98	0.14	1.00
		h_o(mg/g.min)	4.31	8.95	7.41	113.74	19.21	108.03
		RMSE	1.33	0.64	0.32	0.12	0.23	0.24
Elovich	$qt = \beta ln\ (\alpha\beta t)$	α (mg/g.min)	59.18	$3.88x10^5$	$1.4x10^4$	$2.7x10^8$	$5.47\ x10^3$	$8x10^7$
		β (g/mg)	1.02	0.49	0.63	0.35	0.65	0.36
		RMSE	1.38	0.55	0.59	0.29	0.46	0.32
Intraparticle diffusion	$qt = K_{IPD}.\ t^{1/2} + C$	k_{IPD}	4.72	6.17	6.19	6.99	5.76	6.76
		C	0.51	0.25	0.28	0.066	0.30	0.09
		RMSE	1.37	0.56	0.71	0.15	0.62	0.20
Brouers-Sotolongo fractal kinetics	$q_{n,a}(t) = qe[1 - [1 + [n$	qe (mg/g)	9.29	19.60	7.71	7.48	7.44	15.50
		n	1.01	1.23	1.00	3.06	281.49	1.40
		τ	$1.18x10^{-4}$	1.67	0.016	0.22	34.02	1.72
		α	0.45	0.099	1.31	0.51	1.71	0.04
		RMSE	1.63	0.71	0.31	0.15	0.21	0.27

qe and qt are the amounts adsorbed at equilibrium and time, t (mg/g), k_1 is the first order rate constant (g/mg.min) and t is the time in minutes, k_2 is the second order rate constant (g/mg.min), k_{IPD} is the intraparticle diffusion constant and C indicates the boundary layer thickness between the adsorbate and adsorbent, τ is the time needed to adsorb half of the equilibrium quantity in

minutes; a is the time variation of rate constant; n is the fractional order of adsorption, qe is the amount of adsorbate take up at equilibrium in mg/g and qt is the amount of adsorbate taken up at time, t in mg/g.

Table S3: Thermodynamics parameters for the adsorption of CIP and TET onto KCB-A, KCB-B and KCB composite adsorbents

Parameter	**CIP**			**TET**		
	KCB	**KCB-A**	**KCB-B**	**KCB**	**KCB-A**	**KCB-B**
ΔH (KJ/mol)	142.835	70.721	-19.078	-58.663	-139.983	-57.226
ΔS (J/mol.K)	0.509	0.249	-0.018	-0.436	-0.166	-0.174
ΔG (KJ/mol)						
298 K	-3.371	-3.033	-4.319	-1.855	-3.427	-1.608
308 K	-4.089	-3.925	-3.912	-4.634	-2.124	-1.514
318 K	-5.342	-4.354	-4.385	1.723	2.088	2.126