Insights into the Simultaneous Sorption of Ciprofloxacin and Heavy Metals Using Functionalized Biochar

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Supplementary data

Adsorption of contaminants onto raw biochar

To generate CH-BB, suitable raw biochar had to be chosen. Biochar's feedstock strongly depends on pollutants' adsorption properties [1]. The details of their fabrication are presented in Table S1.

It is associated with different functional groups that could potentially attract the contaminants, as shown in Figure S1. Hence, the comparison of adsorption capacity between PW-BC, AS-BC, and PM-BC was carried out. The results are presented in Table S3. All tested biochars were able to adsorb CIP and heavy metals. PM-BC exhibited the highest adsorption capacity for CIP, which can be assigned to its properties such as high surface area [2]. The π-π interaction between CIP and PM-BC functional groups possibly contributed to antibiotic adsorption [1]. In a previously reported study, a higher removal efficiency was obtained due to adsorption onto PM-BC than PW-BC for another pharmaceutical, diclofenac [2]. On the other hand, PM-BC and PW-BC had the same adsorption capacity for Pb. Almost 100% of this metal was adsorbed onto both biochars, while only 72% of Pb was adsorbed onto AS-BC. PW-BC was also more efficient to remove As from the solution. The potency of PW-BC to adsorb As is consistent with previous reports [3]. AS-BC had the highest adsorption capacity towards Cd ions. Based on the overall results, the PM-BC was selected for the fabrication of CH-BB.

Effect of pH on adsorption onto CH-BB

The influence of pH (5.0-9.0) on adsorption capacity was tested for each contaminant, where the initial concentration was 10 mg/L for CIP, As, Cd and 1 mg/L of Pb. All experiments were conducted at room temperature (20±2°C), 150 rpm in an orbital shaker (PSU-20i Multi-functional Orbital Shaker, Biosan). The results are presented in Figure S0. The tested pH range had no significant effect on the removal of CIP (p-value = 0.104) and Pb (p-value = 0.114). For Cd and As, the optimum pH for removal was found to be 6.0 (Fig. S0). For CIP, the results are consistent with the report of Afzal et al. (2018), who also tested CIP removal efficiency of chitosan beads [4]. CIP has two main ionizable groups, carboxylic (pK_{a1} 6.09) and piperazinyl (pK_{a2} 8.74), which makes the compound amphoteric. In the tested range of pH, CIP is present in the solution as zwitterion (CIP±), hence it can adsorb onto CH-BB when its surface is protonated (pH<6) or negatively charged (pH>6) [5]. Moreover, a further increase in pH would result in a decrease of CIP^- adsorption potency due to the higher concentration of CIP^-, as previously suggested [4, 6].

At around pH 6, the functional groups of CH-BB containing oxygen are protonated, and they can attract most of the metals. Moreover, the presence of the amine group of chitosan (pK_a 6.5) increases the number of active sites [7-9]. The adsorption capacity towards As and Cd decreased with the increase of pH above 6. At the tested pH, As is present mostly as $H_2AsO_4^-$, however, due to its speciation, it is not certain if this main form of As was the one that was adsorbed onto CH-BB surface [10]. In the case of Cd, the adsorption capacity increased significantly from pH 5 to 6 (p-value = 0.021) and then started to decrease gradually. Generally, at higher pH, the adsorption capacity decreases due to the generation of soluble hydroxylated complexes of the metal ions.

References

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Tables

Table S1. Production details of used biochars.

Type of biochar	Composition	Pyrolysis procedure
Pinewood biochar (PN-BC)	softwood mix of white pine wood (80% v/v), spruce and fir (20% v/v)	525 ± 1 °C, atmospheric pressure, 2 min, an oxygen-free environment
Almond shell biochar (AS-BC)	Almond shells	520 ± 1 °C, 4 h
Pig manure biochar (PM-BC)	solid fraction of pig slurry	400 ± 1 °C, 2 h at 15 °C min^{-1} in the presence of nitrogen at a flow rate of 2 L min^{-1} during heating

Table S2. Metals concentration leached from biochars and CH-BB. All concentrations are given in μg/L.

Metal	PM-BC	PW-BC	AS-BC	CH-BB
Al	ND	ND	ND	356.9
As	9.7	8.7	6.4	3.9
Be	2.2	1.3	1.6	0.9
Ca	1185.0	2670.7	ND	ND
Cd	0.6	0.3	0.2	0.3
Co	1.2	0.8	0.6	0.4

K	127566.3	15123.3	250530.9	ND
Mg	2933.9	386.2	621.5	914.7
Mn	ND	188.6	ND	8.1
Mo	2121.2	4564.8	2607.4	6451.5
Na	16112.1	ND	ND	5107.7
Ni	1.5	5.4	4.0	9.3
P	4003.4	405.8	2377.1	72.6
Se	88.9	99.6	8.2	90.1
Sr	5.9	14.5	2.9	2.1

Abbreviations: PM-BC – pig manure biochar; PW-BC – pinewood biochar; AS-BC – almond shell biochar; CH-BB – chitosan-biochar beads; ND – not detected.

Table S3. Adsorption capacity of the tested adsorbents; pH 6.0, 150 rpm, 48 h.

Contaminant (initial concentration [mg/L])	Adsorption capacity [mg/g]		
	PM-BC	**PW-BC**	**AS-BC**
Ciprofloxacin (10)	1.36±0.02	1.05±0.08	1.23±0.02
As (10)	0.24±0.24	0.77±0.15	0.56±0.19
Cd (10)	4.88±0.41	1.06±0.08	6.34±0.72
Pb (1)	0.99±0.004	0.99±0.001	0.72±0.07

Abbreviations: PM-BC – pig manure biochar; PW-BC – pinewood biochar; AS-BC – almond shell biochar.

Table S4. Kinetic and adsorption models and their parameters.

Model	Equation	Ref.	Parameters
Pseudo-first order (nonlinear)	*Eq. (S1)* $q_t = q_e(1 - e^{k_1 t})$	[11]	a_{RP} [(mg/L)$^{-g}$]: Redlich-Peterson constant α [mg/g x h]: initial rate constant β [mg/g]: desorption constant C_0 [mg/L]: initial concentration of pollutant g: exponent (ranges between 0 and 1) I: thickness of the boundary layer k_1 [1/h]: the rate constant of pseudo-first-order adsorption k_2 [g/mg h]: the rate constant of pseudo-second-order adsorption K_F [(mg/g)(L/mg)$^{1/n}$]: the Freundlich adsorption constant K_L [L/mg]: the Langmuir adsorption constant K_{RP} [L/g]: Redlich-Peterson constant k_p [mg/g h$^{1/2}$): the intraparticle diffusion rate constant n: the empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material (dimensionless) q_e [mg/g]: the adsorption capacity at equilibrium q_m [mg/g]: complete monolayer adsorption capacity q_t [mg/g]: the adsorption capacity at time t R_L : equilibrium parameter t [h]: contact time
Pseudo-second order (nonlinear)	*Eq. (S2)* $q_t = \frac{q_e^2 k_2 t}{1+k_2 q_e t}$	[12]	
Elovich (nonlinear)	*Eq. (S3)* $q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t)$	[13]	
Intraparticle diffusion	*Eq. (S5)* $q_t = k_p t^{1/2} + I$	[14]	
Langmuir	*Eq. (S7)* $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$ $R_L = \frac{1}{1 + K_L q_m C_0}$	[15]	
Freundlich	*Eq. (S10)* $q_e = K_F C_e^n$	[16]	
Redlich–Peterson	*Eq. (S12)* $q_e = \frac{K_{RP} C_e}{1+a_{RP} C_E^g}$	[17]	

Table S5. Comparison of targeted heavy metals.

Metal	**As**	**Cd**	**Pb**
Type	Metalloid	Transition metal	Post-transition metal
Electron configuration*	[Ar] $4s^2 3d^{10} 4p^3$	[Kr] $5s^2 4d^{10}$	[Xe] $6s^2 4f^{14} 5d^{10} 6p^2$
Electronegativity (Pauling Scale) *	2.18	1.69	2.33
Atomic radius (van der Waals) [pm]*	185	158	202
WHO guideline (drinking water) [µg/L]	10	3	10

*Based on PubChem database.

Figures

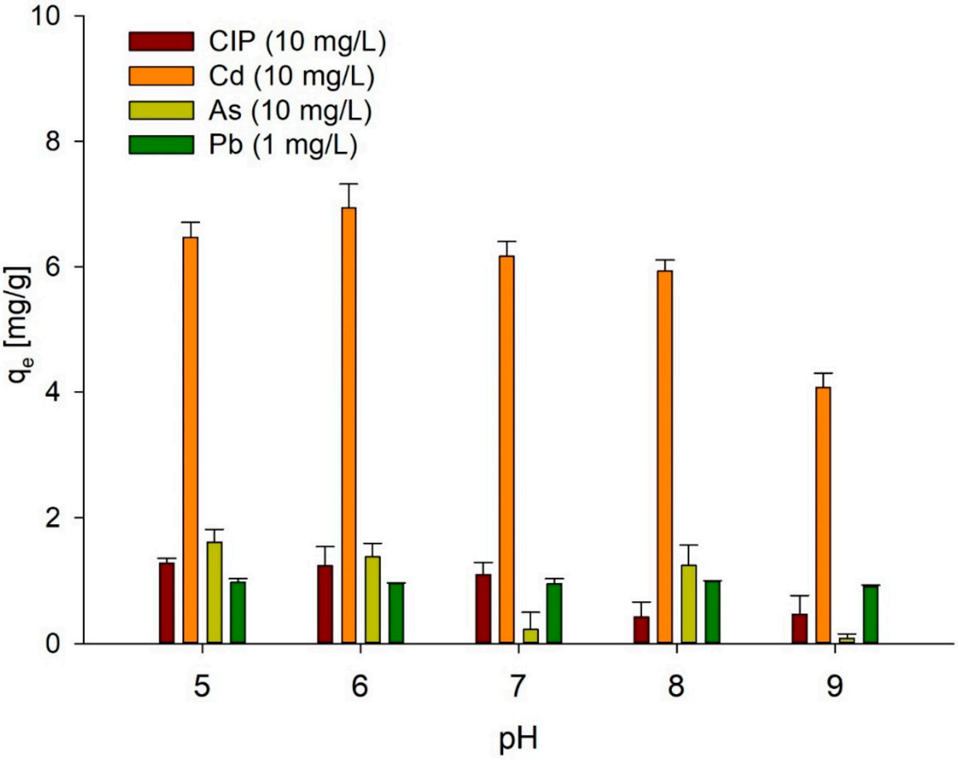

Figure S1. FTIR spectra of tested biochars; PW-BC pinewood biochar, PM-BC pig manure biochar, AS-BC almond shell biochar.

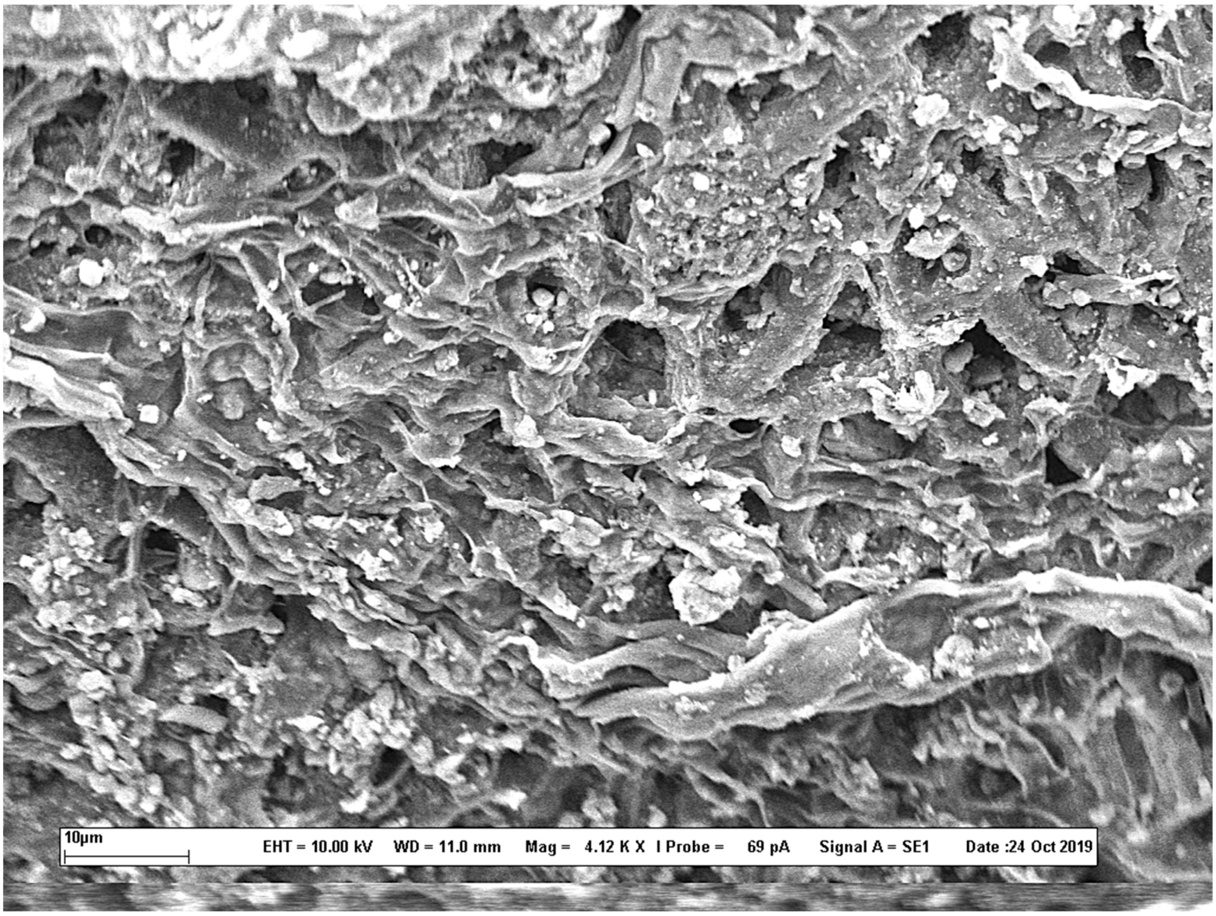

Figure S2. SEM images of pig manure biochar.

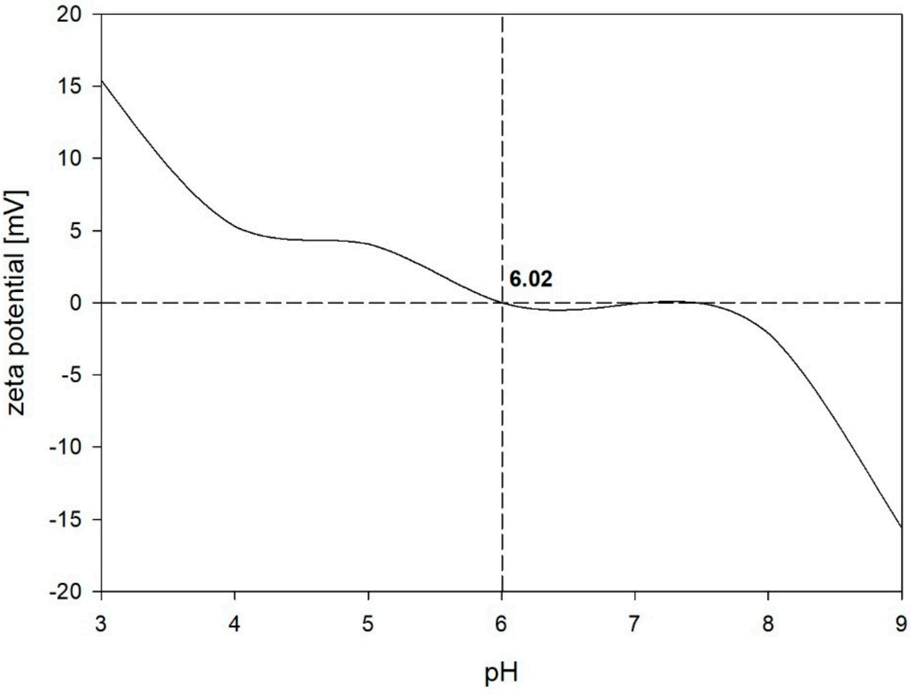

Figure S3. The isoelectric point of CH-BB.

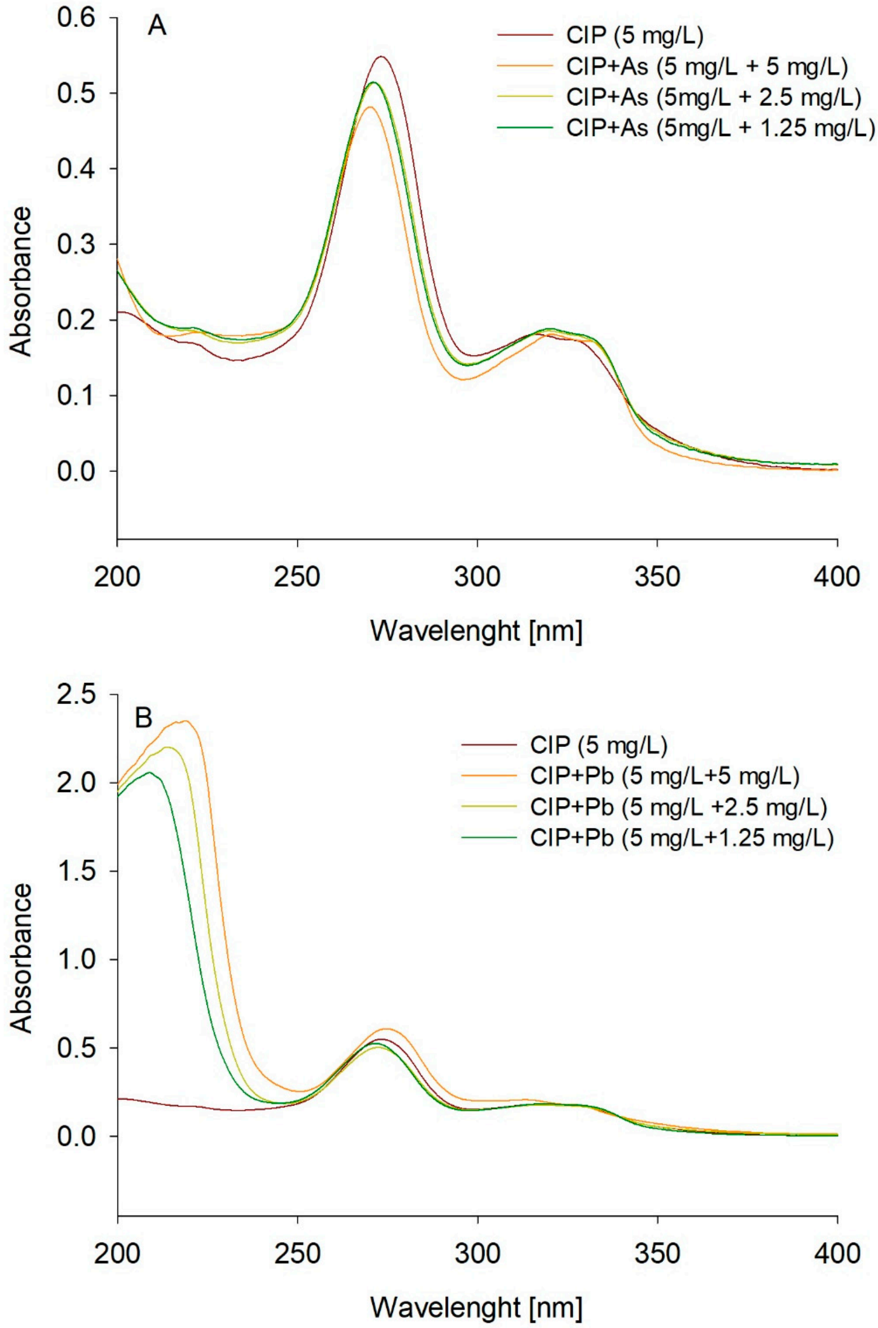

Figure S4. UV-Vis absorption spectra of ciprofloxacin (CIP) in the presence of different concentrations of A. As; B. Pb.