



Removal of benzotriazole derivatives by biochar: Potential environmental applications[☆]

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ABSTRACT

Benzotriazole and its derivatives (BTAs) are commonly present in wastewater due to their extensive use in industrial processes, yet their removal is still unexplored. Here, we test the removal of these pollutants using two functionalised biochars, synthesised from wild plum (WpOH) and apricot (AsPhA) kernels. The aim of this work was to optimise the adsorption process against various BTAs (i.e., benzotriazole (BTZ), 4-hydroxy-1H-benzotriazole (OHBZ), 4-methyl-1H-benzotriazole (4 MBZ), 5-methyl-1H-benzotriazole (5 MBZ), 5-chloro-1H-benzotriazole (ClBZ), 5,6-dimethyl-1H-benzotriazole (DMBZ)), and determine the adsorption mechanisms at play, using real wastewater matrices. Batch studies showed that the optimal adsorption pH ranged between 4 and 6 for WpOH and AsPhA, respectively, and equilibrium was reached after 240 min. The kinetic models that best described the adsorption process were in the following order: Elovich model > pseudo-second order model > pseudo-first order model. The equilibrium data showed the highest correlation with the Freundlich isotherm, indicating multilayer adsorption. The maximum adsorption capacity obtained in mixtures was 379 mg/g on WpOH and 526 mg/g on AsPhA. The mechanistic work revealed that the BTAs became bound to the biochar primarily through H-bonding, n- π and π - π EDA interactions. In wastewater, obtained before and after conventional treatment, the concentration of OHBZ and BTZ was reduced by >40%, while the concentration of the other compounds studied fell below the detection limit (~2.0–90 ng/L). Finally, using a *Vibrio fischeri* assay, we showed that adsorption onto AsPhA significantly reduced the relative toxicity of both raw and treated wastewater.

1. Introduction

Benzotriazole and the various derivatives (BTAs) thereof, are considered emerging environmental contaminants given their potentially toxic effects in the environment and on human health. These compounds are commonly found in industrial and municipal wastewater effluents, and therefore have a direct pathway into receiving surface waters via wastewater treatment plants (WWTPs). WWTPs do not routinely apply treatment methods that would provide complete elimination of these pollutants (Rueda-Marquez et al., 2020). BTAs are

heterocyclic compounds, considered as high-production volume chemicals, widely used in multiple products and industrial applications. They are used in anti-corrosive agents in industrial fluids, in dishwasher detergents, de-icing fluids, cooling systems, and in hydraulic fluids, while less polar derivatives are used as UV stabilisers in plastics and cosmetics (Maceira et al., 2018; Shi et al., 2019). These compounds are likely to reach the environment due to their polarity and water solubility, and BTAs have been identified in wastewater (Loi et al., 2013), surface and groundwater (Serra-Roig et al., 2016), drinking water (van Leerdam et al., 2009), sewage sludge (Herrero et al., 2014), and in outdoor air

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particles (Maceira et al., 2018). Concentrations of BTAs are generally low in surface and groundwater samples (in the ng/L range), while in wastewaters they can occur in the µg/L range (Wang et al., 2023).

Various techniques have been applied to remove BTAs from wastewater, such as: photocatalysis (Xu et al., 2013), ozonation (Dai et al., 2017), biological processes (Mazioti et al., 2015), adsorption (Marszałek et al., 2022) and combined advanced oxidation (Sichel et al., 2011). Of these, adsorption is a cost-effective and attractive method as it does not require expensive equipment or result in the generation of additional toxic or harmful by-products (Pap et al., 2021a). The efficiency of adsorption can be very high, even at low concentrations, but the price of commercially available activated carbon is also high (Gvoic et al., 2022). Recently, alternative (cheaper) adsorbents have been applied for BTA removal, including biologically activated carbon (Piai et al., 2020), oak sawdust biochar (L. Wu et al., 2022), sludge-biochar composites (Cheng et al., 2022), magnetised biochar (Hasanzadeh et al., 2022) and many others. Biochar has several obvious advantages as an adsorbent, such as a large specific surface area, high feedstock availability (i.e., if waste lignocellulosic biomass is used, as here), low-cost, and structural stability. Various biochars have been shown to exhibit high BTA affinity via different binding sites (Bian and Shao, 2023).

The aim of this study was to compare the overall performance of two functionalised biochars to remove BTAs. One biochar was synthesised using KOH/microwave assisted pyrolysis of wild plum kernels (WpOH), while a second was produced via conventional pyrolysis using phosphoric acid to functionalise material from waste apricot kernels (AsPhA). The effectiveness of both was examined in batch conditions, while changing various operating parameters (pH, contact time, pollutant concentration and temperature). The morphology, structure, and chemical composition of the prepared WpOH and AsPhA biochar was fully characterised before and after adsorption. Subsequently, real wastewater was tested to examine possible matrix effects. In addition, desorption of the BTAs in different media was also investigated, to evaluate reusability. Finally, the improved toxicological profile of the effluent showed that the treated water was safe to discharge. This work holistically examines two novel biochars, understands their behaviour at the molecular level (in terms of BTA removal) and seeks to maximise their performance.

2. Materials and methods

2.1. Synthesis of the biochars

Synthesis of WpOH was undertaken as described in our previous study (Paunovic et al., 2019). AsPhA was synthesised based on the methodology shown in Turk Sekulic et al. (2018).

2.2. Materials, analytical methods and wastewater effluent

Solid standards of the analytes used in this study were purchased from Sigma-Aldrich, USA (1H-benzotriazole (BTZ), 4-hydroxy-1H-benzotriazole (OHBTZ), and 5-chloro-1H-benzotriazole (ClBTZ)), and from Fluka, Switzerland (4-methyl-1H-benzotriazole (4 MBZ), 5-methyl-1H-benzotriazole (5 MBZ), and 5,6-dimethyl-1H-benzotriazole (DMBTZ)). The structure and properties of the BTAs are shown in Table S1. Ultrapure water was prepared using a Milli-Q® system (Millipore, USA). The HPLC grade solvents, acetonitrile (Fisher Chemical, UK) and methanol (J. T. Baker, UK), were used. Other chemicals were high purity and from various producers: formic acid (Sigma-Aldrich; USA), 25% NH₃ (Grammol; Croatia), HCl (Honeywell; USA), NaOH (Merck; USA), potassium hydroxide (KOH) (Fisher Scientific; USA).

Solid-phase extraction cartridges used were Oasis MAX (500 mg), supplied by Waters (Milford, MA, USA). BTA solutions (from the adsorption experiments) were quantified using high-performance liquid chromatography (HPLC) coupled to a diode-array detector (DAD), and through triple quadrupole mass spectrometry (LC-MS/MS) (Kraševac

and Prosen, 2021). Detailed methods are shown in Supplementary Materials S1.

Municipal wastewaters (24 h composite samples) were taken at the Central WWTP in Ljubljana, Slovenia, before and after standard treatment. Samples were collected in pre-cleaned HDPE bottles and stored at −20 °C. The chemical characteristics of the influent and effluent are presented in Table S2.

2.3. Biochar characterisation

The WpOH and AsPhA biochars were characterised using scanning electron microscope (SEM), a nitrogen gas automatic surface analyser, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Details of the characterisation methods are shown in Supplementary Materials S1.

2.4. Adsorption and desorption experiments

Initial screening experiments were performed with four different adsorbents: The WpOH and AsPhA biochars, and two other carbonaceous adsorbents synthesised from plum and cherry kernels - PPhA (Pap et al., 2017) and CScPA (Pap et al., 2016), respectively. The pyrolysis conditions for PPhA and CScPA were identical to that used for AsPhA, but the feedstock was different.

In experiments, 20 mg of each biochar was mixed in an Erlenmeyer flask with 50 mL of aqueous solution containing 0.1 mg/L of OHBTZ, BTZ, 4 MBZ, 5 MBZ, ClBTZ, and DMBZ in mixture, at pH 6–7. The pH was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. For this purpose, a mechanical flat-bed shaker was used at 90 rpm at 22 °C for 180 min.

Later, when optimising the performance of WpOH and AsPhA specifically, the following experimental conditions were used to assess the effect of pH on adsorption (of BTAs), with BTA solutions prepared at 1 mg/L in Erlenmeyer flasks, a biochar dose of 0.4 g/L, and pH controlled in the range of 2–9. Flasks were then placed on a mechanical flat-bed shaker at 90 rpm for 240 min at room temperature (22 °C). After filtration, using a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter, BTA removal *R* (%), and adsorption capacity *q_e* (mg/g), were determined using:

$$R (\%) = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (2)$$

where *C₀* was the initial BTA concentration, *C_e* was the residual concentration (mg/L), *V* the volume of solution (mL) and *m* the mass of biochar (mg). More details about the experimental conditions are shown in Supplementary Materials S2.

BTA desorption experiments were conducted by adding 200 mg of biochar to 500 mL of a solution containing 5 mg/L of each BTA as a mixture (total BTAs concentration - 30 mg/L), and then shaking for 240 min. The resultant BTA-loaded biochar was then separated from the suspension by filtration, then desorbed using 3 different solutions and ultrasound, separately, (a) 0.1 M NaOH, (b) 0.1 M HCl, and (c) methanol – using a liquid:solid ratio of 2500 mL/g (i.e., 20 mg in 50 mL of eluent) at 22 °C. After a 4 h contact time, eluent supernatants were removed and the BTA concentrations determined. At a given time, *t*, the desorption efficiency (*d_E* (%)) was calculated using the following:

$$d_E = \frac{q_d}{q_a} \cdot 100 \quad (3)$$

where *q_d* (mg/g) is the amount of BTA desorbed, and *q_a* (mg/g) is the adsorption capacity. Similar experimental procedures were adopted using real wastewater as the liquid matrices (raw wastewater and wastewater after final treatment) to more realistically assess the likely

percentage removal and the selectivity of the WpOH and AsPhA. The adsorptive uptake was evaluated by adding 20 mg of biochar to 50 mL of wastewater in 150 mL conical flasks. The mixture was agitated at 22 °C for 240 min at an agitation speed of 90 rpm, and no pH adjustment was adopted.

2.5. Toxicological potential of the wastewater samples

The relative toxicity of real wastewater solutions, naturally containing low levels of BTAs, before and after adsorption treatment with biochar, was determined using the luminescent marine bacteria *V. fischeri*. BTAs were not artificially added (spiked) into solutions. For these toxicity measurements, biochar (20 mg of WpOH and AsPhA) was added to 50 mL of wastewater in Erlenmeyer flasks. The pH of the solutions was not adjusted. Flasks were then placed on a shaker at 90 rpm for 240 min at room temperature (22 °C). 40 mL of sample was then filtered off and measured into plastic tubes and the pH adjusted to pH 7 prior to toxicity testing (with hydrochloric acid or sodium hydroxide to avoid possible effects due to pH variation). Osmolality of the sample was also measured, using a vapour pressure osmometer (K-7000, Knauer) and adjusted to match that of a 2% (w/v) NaCl solution.

The toxicity of these solutions was then determined using freeze dried luminescent bacteria (*V. fischeri*) with a LUMISTox system (Dr Lange) according to ISO 11348-3 (ISO, 2007). The toxicity endpoint was determined as reduced luminescence emission.

An aliquot of *V. fischeri* was added to a test tube, in duplicate, and luminescence was measured immediately. Next, the wastewater sample was added to the vial and the vial held at 15 ± 1 °C. The luminescence of the bacteria was measured again after 30 min exposure. The inhibition of luminescence was calculated using the LUMISoft IV software model. Blank tests were also performed using a solution of 2% w/v sodium chloride.

Note that this test was simply used to test the 'relative' toxicity of real (un-spiked) wastewater pre- and post-treatment with biochar. As such, the results were not specific to BTA levels and are instead representative of the 'overall' change in toxicity of wastewater solutions following treatment with these biochars.

2.6. Modelling and statistics

Kinetic, isotherm and thermodynamic models used in this study are shown in Supplementary Material S3 and Table S3. Each adsorption experiment was carried out in triplicate, and the data reported as the mean. Coefficient of determination (R^2), the root mean square error (RMSE) and the nonlinear chi-square test (χ^2) were used to analyse the errors within the data (see Supplementary Material S3).

3. Results

3.1. Initial screening of adsorbents

Four different biochars were initially tested, with BTA removal efficiencies generally >50%, and several >90% (Fig. S1). Considering the highest S_{BET} value, AsPhA was the most efficient biochar, demonstrating removal efficiencies >90% for all target compounds, except for ClBZ. CSaP also demonstrated a high removal percentage, while PPhA was the least efficient, but still >70%. WpOH had the lowest efficiency, but was still considered satisfactory with >60% removal for most BTAs. Alongside AsPhA, WpOH was chosen for further study – the main reason being that WpOH was prepared in a completely different way (KOH assisted microwave pyrolysis) to the other biochars. As such, the results derived during optimisation would be significant for further research and application of this material.

3.2. Influence of process conditions

Experiments were performed to optimise BTA removal using the two selected biochars (AsPhA and WpOH), while varying contact time, initial adsorbate concentration, temperature, and solution pH.

The influence of pH on adsorption was plotted as a function of removal efficiency (%) (Figs. S2a–b), with higher removal observed at lower pH. For WpOH, removal efficiency was very high between pH 2 to 4, but for AsPhA it increased up to pH 6 and then decreased slightly at pH values > 7. Although the highest removal efficiencies were observed at low pH, in subsequent experiments we used pH 4 for WpOH and pH 6 for AsPhA, to reduce overall acidity and replicate more common/realistic environmental conditions.

The time dependent adsorption process is presented in Figs. S2c–d. For both biochars, adsorption was initially rapid and spontaneous (during the first 60 min). After which, adsorption slowed and reached equilibrium at 240 min for WpOH, while the AsPhA kinetic profile was different, with slower saturation, likely due to its much larger porosity whereby pore diffusion could be a rate limiting step.

Adsorption of individual BTA compounds (OHBZ, BTZ, 4 MBZ, 5 MBZ, ClBZ, and DMBZ) was investigated at various initial concentrations, as shown in Figs. S2e–f. The equilibrium adsorption capacity was highly dependent on the initial BTA concentration used for both biochars, with the highest value observed at an initial concentration of 50 mg/L. This is because the high BTA concentration provides a higher concentration gradient and thus driving force to overcome mass transfer resistance. For adsorption with WpOH, the highest adsorption capacity was observed for ClBZ (98.1 mg/g) with a removal efficiency of 78.4%. AsPhA was found to be the most efficient option, with the highest adsorption capacity for DMBZ (120 mg/g) and a high removal efficiency (96.3%).

3.3. Adsorption kinetics

The interaction kinetics and mass transfer of BTAs onto WpOH and AsPhA are illustrated in Fig. 1 a-b and Figs. S3a–b, respectively. The experimental data were fitted and analysed using the pseudo-first order (PFO) model (Lagergren, 1898) (fitting not shown on Fig. 1a and b), pseudo-second order (PSO) model (Blanchard et al., 1984), Elovich model (Roginsky and Zeldovich, 1934) and the Weber-Morris intraparticle diffusion model (W-M) (Weber and Morris, 1963). R^2 , RMSE and χ^2 were calculated to assess the goodness-of-fit (with the model constants summarised in Table 1). Considering the highest R^2 (0.99 for WpOH and 0.95–0.99 for AsPhA), lowest χ^2 (0.01–0.03 for WpOH and 0.07–3.49 for AsPhA) and RMSE (0.11–0.17 for WpOH and 0.26–1.87 for AsPhA) values for both biochars, it can be concluded that the Elovich model best describes the kinetic data. The PSO models also had high R^2 values, low χ^2 and RMSE values, and the calculated $q_{t,cal}$ results were close to the experimental data $q_{t,exp}$. Using the data obtained from the PSO model, we determined the time necessary for WpOH and AsPhA to remove 50% ($t_{1/2}$) of the BTA molecules from solution. The $t_{1/2}$ values for WpOH were between 1 and 3.6 min, while for AsPhA, they were between 1.1 and 11.9 min. The uptake of these BTAs was therefore fast.

On microporous biochar, pore diffusion is generally a slow process which could lower the rate of BTA adsorption onto active sites inside biochar pores (Liu et al., 2021). In this study, the kinetic pattern for BTA adsorption showed a strong linear dependency ($R^2 = 0.96–0.78$) (see Figs. S3a–b for both biochars). This indicates that intraparticle surface diffusion plays a significant role in the adsorption process. The average pore size for WpOH was smaller when compared to AsPhA (see below), which in turn would have influenced the k_i (mg/g min^{1/2}) values for all BTAs, i.e., they were lower for WpOH ($k_i = 0.07–0.11$) than for AsPhA ($k_i = 0.12–0.45$).

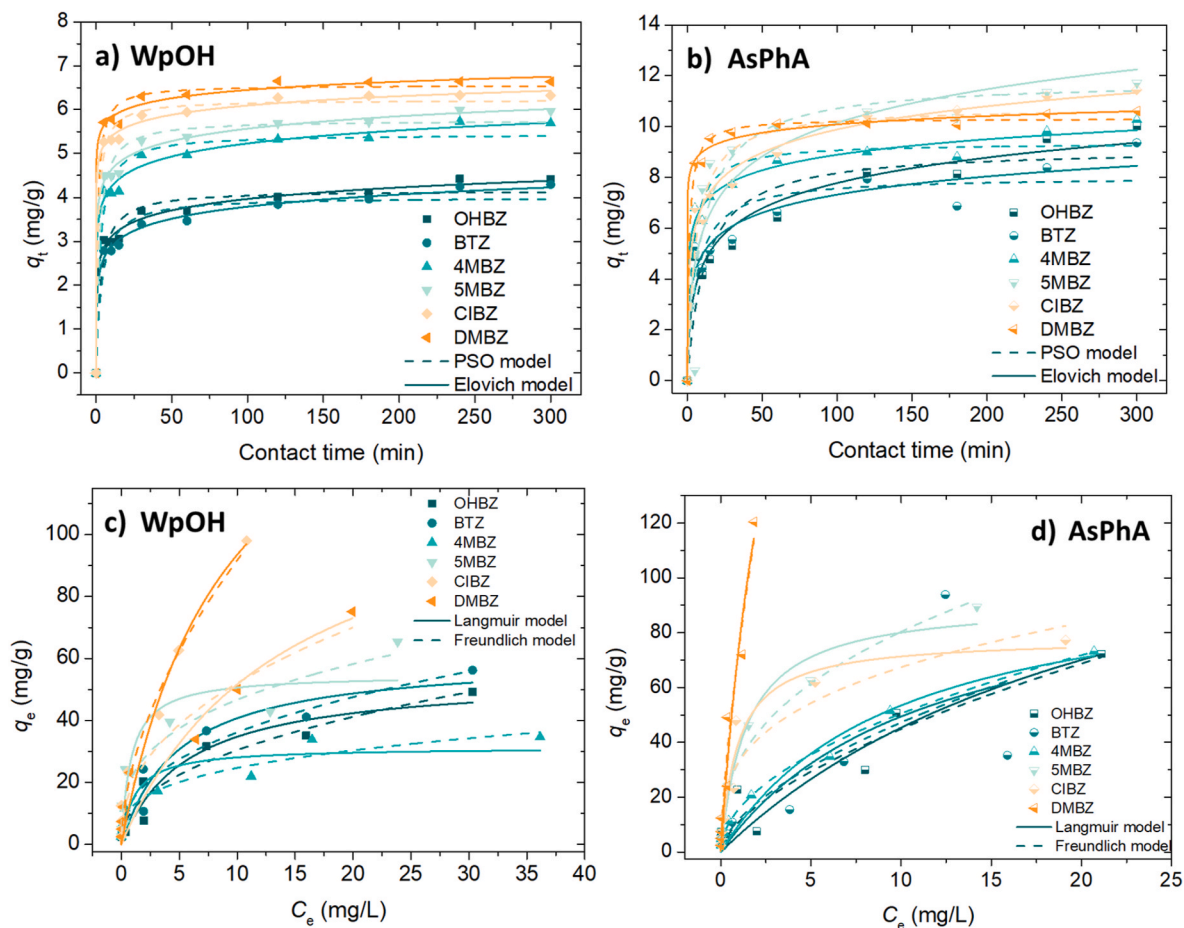


Fig. 1. Interaction kinetics (a–b) and isotherms (c–d) modelling the BTA adsorption process (initial pH: 4 (a) and 6 (b); agitation time: 5–300 min; initial concentration: 1–50 mg/L; agitation speed: 90 rpm; temperature: 22 °C; biochar dose: 0.4 g/L).

Table 1

Interaction and diffusion kinetic parameters for the adsorption of six BTAs onto WpOH and ApPhA.

Biochars		WpOH						ApPhA					
Compounds		OHBZ	BTZ	4 MBZ	5 MBZ	CIBZ	DMBZ	OHBZ	BTZ	4 MBZ	5 MBZ	CIBZ	DMBZ
$q_{t,exp}$ (mg/g)		4.41	4.29	5.69	5.97	6.32	6.63	10.0	9.36	10.3	11.7	11.4	10.6
Pseudo-first order model	$q_{t,cal}$ (mg/g)	3.96	3.80	5.19	5.51	6.01	6.36	8.40	7.51	8.88	10.8	10.1	10.0
	k_1 (min^{-1})	0.19	0.17	0.23	0.26	0.37	0.41	0.06	0.11	0.18	0.08	0.12	0.33
	R^2	0.88	0.87	0.90	0.92	0.96	0.97	0.76	0.75	0.87	0.89	0.83	0.97
	RMSE	0.44	0.44	0.52	0.49	0.38	0.36	1.47	1.32	1.05	1.41	1.40	0.52
	χ^2	0.19	0.20	0.27	0.24	0.15	0.13	2.17	1.74	1.10	2.00	1.95	0.27
Pseudo-second order model	$q_{t,cal}$ (mg/g)	4.16	4.01	5.44	5.76	6.22	6.56	9.14	8.03	9.36	11.8	10.8	10.3
	k_2 (g/mg min)	0.08	0.07	0.07	0.08	0.12	0.15	0.01	0.02	0.03	0.01	0.02	0.08
	$t_{1/2}$ (min)	3.07	3.60	2.48	2.13	1.29	1.05	11.9	6.21	3.28	10.1	5.63	1.29
	R^2	0.95	0.95	0.96	0.97	0.99	0.99	0.86	0.85	0.94	0.88	0.92	0.99
	RMSE	0.29	0.29	0.33	0.30	0.23	0.22	1.13	1.03	0.72	1.51	0.95	0.29
Elovich model	χ^2	0.08	0.08	0.11	0.09	0.05	0.05	1.27	1.06	0.52	2.29	0.91	0.08
	α (mg/g min)	146	56.1	862	3545	1.40×10^6	5.60×10^7	3.11	12.5	219	3.78	24.3	8.76×10^6
WB intraparticle diffusion model	β (mg/g)	2.67	2.52	2.34	2.46	3.27	3.68	0.69	0.97	1.14	0.52	0.76	2.12
	R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.95	0.93	0.98	0.81	0.98	0.99
	RMSE	0.14	0.11	0.17	0.14	0.11	0.14	0.69	0.69	0.39	1.87	0.43	0.26
	χ^2	0.02	0.01	0.03	0.02	0.01	0.02	0.47	0.48	0.15	3.49	0.18	0.07
	k_i ($\text{mg/g min}^{1/2}$)	0.10	0.10	0.11	0.10	0.08	0.07	0.38	0.28	0.23	0.45	0.35	0.12
	C (mg/g)	2.84	2.59	3.96	4.37	5.20	5.66	3.42	4.14	6.24	4.87	5.93	8.73
	R^2	0.92	0.96	0.88	0.87	0.83	0.77	0.96	0.87	0.90	0.78	0.95	0.73

3.4. Adsorption isotherms

To further investigate the adsorption process, the equilibrium data were fitted with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models (Dubinin et al., 1947; Freundlich, 1907; Langmuir, 1918). The fitting parameters are listed in Table 2. The best-fit for the models followed the order: Freundlich > Langmuir > D-R. According to the correlation coefficients R^2 , RMSE and χ^2 , the adsorption data for both biochars fitted the Freundlich model better (heterogeneous adsorption), while the Langmuir (monolayer adsorption) and D-R models (pore filling) described the adsorption less satisfactorily (except for BTZ and ClBZ onto AsPhA). The Freundlich isotherm constant $1/n$ values ranged between 0 and 1, indicating that the biochars had favourable adsorption towards BTAs. The average adsorption affinity (K_F) of AsPhA was between 10.9 and 73.8 ((mg/g)/(mg/L)^{1/n}) compared to WpOH at 11.1–25.5 ((mg/g)/(mg/L)^{1/n}), confirming that AsPhA showed better performance for BTA adsorption. The maximum adsorption capacity obtained in mixtures was 379 mg/g on WpOH and 526 mg/g on AsPhA (Fig. S4). The higher $q_{\max, \text{exp}}$ for AsPhA could also be explained by the larger surface area and average pore size. Also, since OHBZ (9.74 nm) has the biggest molecular diameter (Table S1), OHBZ molecules might not readily diffuse into the pores of AsPhA, resulting in the lowest $q_{\max, \text{exp}}$ observed. The relatively good correlation with the D-R model ($R^2 \geq 0.60$) highlights the effect of the highly porous structure of the biochars, whereby adsorption likely occurred via pore filling rather than by layer-by-layer adsorption onto pore walls (Czech et al., 2021).

3.5. Adsorption thermodynamics

Thermodynamic parameters (ΔG° , ΔH° , and ΔS°) are vital when determining the spontaneity of the adsorption process (Cimirro et al., 2022; Lima et al., 2020). From the Langmuir equilibrium constants (K_L), and using the van't Hoff equation, various thermodynamic parameters were calculated (see more details in Supplementary Material S3). The parameters are shown in Table 3 and were calculated using the nonlinear regression method. These showed that the Gibbs free energy (ΔG°) for all BTAs, on both biochars, was negative and consistent, while ΔH° was positive and varied from 31.0 to 49.1 kJ/mol for WpOH and from 14.2 to 38.9 kJ/mol for AsPhA. These results indicated that the adsorption process was spontaneous and endothermic. As displayed in Table 3, the values for changes in enthalpy of adsorption were always positive and <50 kJ/mol - the magnitude of ΔH° is therefore compatible with H-bonding (4–60 kJ/mol), dipole-dipole (0.5–15 kJ/mol) and dispersion interactions (4–40 kJ/mol), i.e., physical adsorption

processes (Chang and Thoman, 2014). ΔS° remained highly positive for all examined conditions and BTAs, highlighting an increase in randomness at the solid–liquid interface (de Azevedo et al., 2023).

3.6. Desorption studies

In terms of the desorption results presented in Fig. 2a and b, it should be noted that the regeneration process was more effective with AsPhA, suggesting that the formed bonds between AsPhA and the BTAs were weaker (and thus more reversible) than for those between WpOH and the BTAs. NaOH was the most efficient desorption agent, with an efficiency >95% for 4 MBZ and 5 MBZ, while for the other BTAs the efficiency is >40% (except OHBZ). HCl, as an acidic matrix, showed the lowest desorption (for AsPhA). Methanol and ultrasound generally desorbed <50% of the BTAs. Desorption of OHBZ was very low for all options. Desorption of BTAs was very low from WpOH, generally <10%, except for 5 MBZ with NaOH, HCl and ultrasound and DMBZ with NaOH.

3.7. Real wastewater and relative toxicity data

For use in more realistic matrices, WpOH and AsPhA were tested using real wastewater samples. The wastewater was not 'spiked' in any way, the 'as sampled' levels of BTAs were simply assessed, and then the biochars applied to reduce these levels. Analysis of BTAs in raw wastewater and in this water after biochar treatment (Table S2) with WpOH showed a significant decrease in BTA concentrations for all investigated compounds, except for ClBZ (Fig. 2c). AsPhA was perhaps slightly more effective in removing low concentrations of BTAs in these real environmental matrices, which was more obvious when treating final effluent (Fig. 2d). However, Fig. 2c and d suggest that the removal of BTAs was slightly more efficient in final wastewater effluent (compared to raw wastewater), perhaps because it is a simpler matrix, with much lower (potentially interfering) COD, BOD and suspended solids (Table S2).

In terms of crude toxicity measurement, luminescent marine bacteria were used, and this showed that the adsorption process reduced the toxicity of raw wastewater (Fig. 2e). AsPhA created the largest improvement in quality, for both raw wastewater and final treated effluent. Initial luminescence inhibition was ~72% for raw wastewater, which reduced to ~29%, while for treated wastewater initial inhibition was ~12% reducing to ~2% after AsPhA treatment. WpOH treatment slightly increased the toxicity of final processed water, although this change was probably not statistically significant.

Table 2
Langmuir, Freundlich and D-R isotherm data for the adsorption of six BTAs onto WpOH and ApPhA.

Biochars		WpOH						ApPhA					
Compounds		OHBZ	BTZ	4 MBZ	5 MBZ	ClBZ	DMBZ	OHBZ	BTZ	4 MBZ	5 MBZ	ClBZ	DMBZ
$q_{\max, \text{exp}}$ (mg/g)		49.2	56.2	34.6	65.4	98.0	75.1	72.2	93.9	73.3	89.5	77.2	120
Langmuir isotherm	$q_{\max}$ (mg/g)	54.3	60.6	31.3	54.8	180	125	154	105	105	91.5	78.1	316
	K_L (L/mg)	0.18	0.20	0.87	1.20	0.11	0.07	0.04	0.09	0.10	0.70	0.11	0.31
	R^2	0.92	0.92	0.84	0.84	0.94	0.87	0.86	0.57	0.96	0.90	0.94	0.93
	RMSE	4.98	5.62	4.99	9.00	8.36	9.16	9.30	20.0	5.10	5.54	6.98	11.1
	χ^2	24.8	31.6	24.9	80.9	69.9	83.9	86.6	400	26.1	30.7	48.7	122
Freundlich isotherm	K_F ((mg/g)/(mg/L) ^{1/n})	11.1	14.5	12.4	22.4	25.5	19.4	10.9	11.8	15.7	33.0	32.9	73.8
	$1/n$	0.44	0.40	0.30	0.32	0.56	0.43	0.61	0.60	0.51	0.39	0.31	0.71
	R^2	0.93	0.95	0.94	0.92	0.96	0.96	0.88	0.55	0.99	0.98	0.90	0.95
	RMSE	4.58	4.61	3.03	6.50	6.65	5.22	8.57	20.3	2.31	4.37	9.21	9.73
	χ^2	20.9	21.2	9.21	42.3	44.2	27.3	73.4	414	5.32	19.1	84.9	94.7
Dubinin-Radushkevich isotherm	q_{DR} (mg/g)	40.7	46.8	31.4	56.5	108	53.7	84.3	69.9	58.6	71.9	70.8	120
	K_{DR} (mol ² /kJ ²) ($\times 10^{-6}$)	1.05	0.96	1.44	1.42	2.35	0.18	9.43	4.16	0.92	0.11	0.14	0.10
	E (kJ/mol)	0.69	0.72	0.59	0.59	0.46	1.66	0.23	0.35	0.74	2.16	1.88	2.19
	R^2	0.84	0.86	0.69	0.66	0.88	0.74	0.80	0.60	0.81	0.88	0.90	0.88
	RMSE	6.86	7.55	7.00	13.1	11.7	13.1	11.0	19.3	11.1	11.1	8.93	14.3
	χ^2	47.1	57.0	49.0	171	137	171	121	372	123	122	79.7	206

Table 3

Thermodynamic parameter data for the adsorption of six BTAs onto WpOH and AsPhA.

Biochar	T (K)	BTAs	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)	Biochar	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
WpOH	295	OHBZ	33.5	220	-31.4	AsPhA	35.3	235	-34.0
	305				-33.6				-36.4
	315				-35.8				-38.7
	295	BTZ	49.1	260	-27.8		38.9	224	-27.3
	305				-30.4				-29.6
	315				-33.0				-31.8
	295	4 MBZ	32.0	209	-29.8		25.5	181	-27.9
	305				-31.9				-29.7
	315				-34.0				-31.5
	295	5 MBZ	46.8	254	-28.1		25.5	195	-28.9
	305				-30.6				-30.8
	315				-33.2				-32.8
	295	CIBZ	31.0	192	-25.6		31.1	193	-29.4
	305				-27.5				-30.4
	315				-29.5				-31.3
	295	DMBZ	40.9	221	-24.4		14.2	146	-25.8
	305				-26.6				-27.7
	315				-28.8				-29.7

3.8. Characterisation of the adsorbents

Surface morphological and textural properties of the WpOH and AsPhA were examined using SEM. The differences between the two biochars can be seen in Fig. 3a–d. Both biochars, WpOH and AsPhA, show a typical porous structure (for lignocellulose-derived biochar). The WpOH surface had an uneven structure, with visible pores of larger and smaller diameter, while the AsPhA surface was quite homogeneous, also with clearly visible deep pores.

The quantitative BET data for both biochars are shown in Table S4. Based on this, it can be noted that the total specific surface area of both biochars decreased during adsorption (WpOH from 601.9 to 170.5 m²/g, and AsPhA from 1098.9 to 462.4 m²/g). Total pore volume also decreased following adsorption (by 41.6% for WpOH and 60.2% for AsPhA), as well as micropore volume (by 71% for WpOH and 81.3% for AsPhA). The total pore volume of micropores and the average pore diameter (~2 nm) was indicative of their micro/mesoporous character.

Fig. 4a shows the XRD data obtained for WpOH and AsPhA. Two broad peaks were obtained at angles of approximately 2 θ = 25° and 2 θ = 43.5° for both biochars. The broad peak at 25° could be allocated to reflection plane C (002), while the peak at 43.5° can be allocated to reflection plane C (100/101) (Turk Sekulic et al., 2019). Both peaks are characteristic of an amorphous structure. For BTAs (and generally for organic pollutant adsorption), an amorphous nature is favourable, since it facilitates the diffusion of molecules into the porous structure (da Silva et al., 2022).

Fig. 4b shows the FTIR data, with the observed peaks before and after BTA adsorption for both biochars. Peaks observed at approximately 3500 cm⁻¹ can be allocated to O–H and N–H groups within carboxyls and phenols. Peaks between 2350 and 2920 cm⁻¹ are assigned as asymmetric stretching of the C–H bond (alkane/alkene groups). Three bands (observed around ~1650, 1050 and 870 cm⁻¹) are attributed to C=O stretching in ester or carboxylic acids and C–O and C–O–C stretching in phenolic and carboxylate groups, respectively. For AsPhA, since it was functionalised with phosphoric acid, some P–O stretching vibrations of PO₄³⁻ (around 1060 cm⁻¹) can be seen in the FTIR spectra. The bands at ~1160 cm⁻¹ could be allocated to hydrogen-bonded P=O derived from the phosphoric acid activation (Cimiro et al., 2022; da Silva et al., 2022; Nguyen et al., 2020; Ninh et al., 2023). The slight changes in oxygen-functional groups on the WpOH and AsPhA surfaces can act as adsorption sites for BTAs through different interactions such as H-bonding and π - π interactions, while C=C bonds can interact through π - π interaction with aromatic contaminants (such as BTAs; (Ninh et al., 2023).

Quantitative analysis of biochar surface chemistry was performed using XPS. The XPS spectra (Fig. 4c) for WpOH and AsPhA showed major

peaks at 284.9, 399.9, 532.2, and 133.1 eV, denoted as C 1s, N 1s, O 1s and P 2p, respectively. The table in Fig. 4c shows the atomic percentage of the main elements on the biochar surface before and after BTA adsorption (note: some other elements, such as Cl, Ca, Na and Si were present on the biochar at <0.5%). The elemental composition of both biochars (Fig. 4c and Table 4) changed slightly after BTA adsorption. High resolution scans for C 1s, O 1s and N 1s are presented for AsPhA to represent changes in the biochar surface functionalities (Fig. 4d–f). The high-resolution spectrum of C 1s (Fig. 4d) is deconvoluted into three peaks, namely: aromatic carbon and aliphatic structures (C–C and C=C; 284.38 eV); the hydroxyl, phenolic, alcohol, or ether groups (C–O; 285.98 eV); and the carboxyl groups (O–C=O; 288.98 eV). The O 1s high-resolution scan (Fig. 4e) can be separated into three peaks at 530.78 eV, 532.68 eV and 535.58 eV, which are delegated to O–C=O, C=O and P=O bonds, C–O and C–P bonds, and to water and chemisorbed oxygen, respectively. These XPS spectra indicate that WpOH and AsPhA had oxygen-rich functional groups. The N 1s high-resolution spectra (Fig. 4f) are divided into two peaks. The peak at 398.58 eV is attributed to –NH₂ and C=N, while the peak at 400.48 eV is attributed to groups such as C–N and N–C=O (Azzam et al., 2022; Chahine et al., 2020; Shi et al., 2022; Q. Wu et al., 2022). After BTA adsorption, the heights of all peaks significantly decreased for O 1s, while for C 1s and N 1s the peaks increased. This implies surface heterogeneity and the formation of different molecular interactions, such as H-bonding, π - π and n - π interactions, which is in line with the results obtained from our FTIR analysis (Feng et al., 2022; Q. Wu et al., 2022).

4. Discussion

The most common adsorption mechanisms on porous solid surfaces are electrostatic interactions, hydrophobic interactions, H-bonding, and EDA interactions. BTAs are polar organic pollutants, which can be found in an ionised form in aqueous solutions and various mechanisms have been used to explain biochar-BTA interactions (Minh and Lee, 2018). One of the most important parameters affecting adsorption is solution pH, since it defines the ionic state (pK_a) of a BTA and the surface charge of the biochar (pH_{pzc}) (Xu et al., 2022). The investigated biochars here had an amphoteric character and therefore their charge, and the mechanisms of adsorption of the BTAs, depended on the pH of the solution. As shown in a previous study (Paunovic et al., 2019), the pH_{pzc} of the WpOH was neutral or slightly basic (7.2). Since the pK_a values of the studied compounds ranged between 7.3 and 8.9 (except for BTZ, which has two pK_a values, 8.2 and 1.6) (Fig. S5), electrostatic interaction was not expected, but adsorption was still present through other interactions and pore filling. The pH_{pzc} of AsPhA was 4.0 (Turk Sekulic et al., 2018), so strong electrostatic interactions may be present between pH 4–7

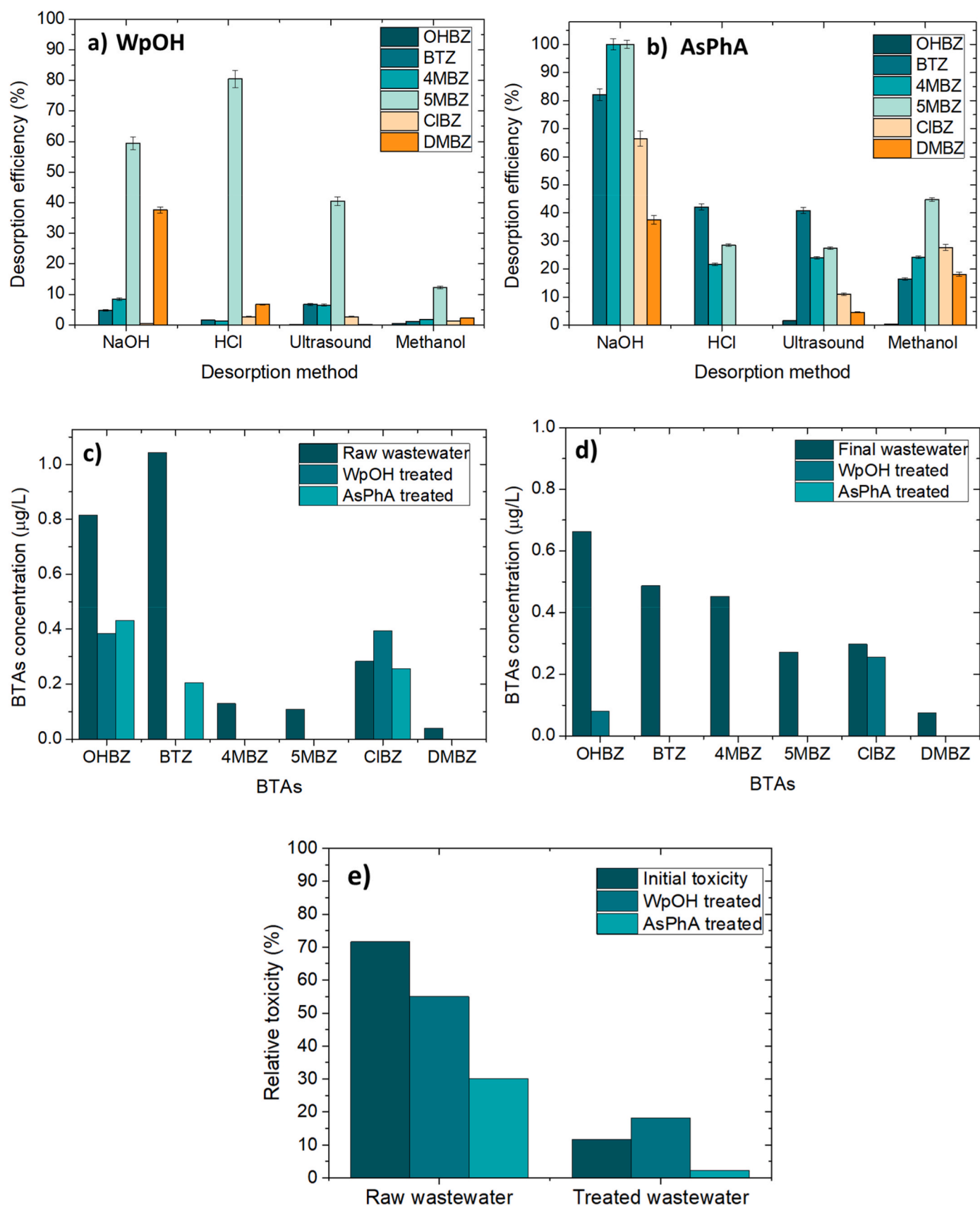


Fig. 2. Desorption study (a–b) for BTAs present on the biochars, and difference in concentration of BTAs in raw (c) and treated (d) wastewater after biochar treatment. Relative toxicity change (e) of the wastewaters before and after the treatments.

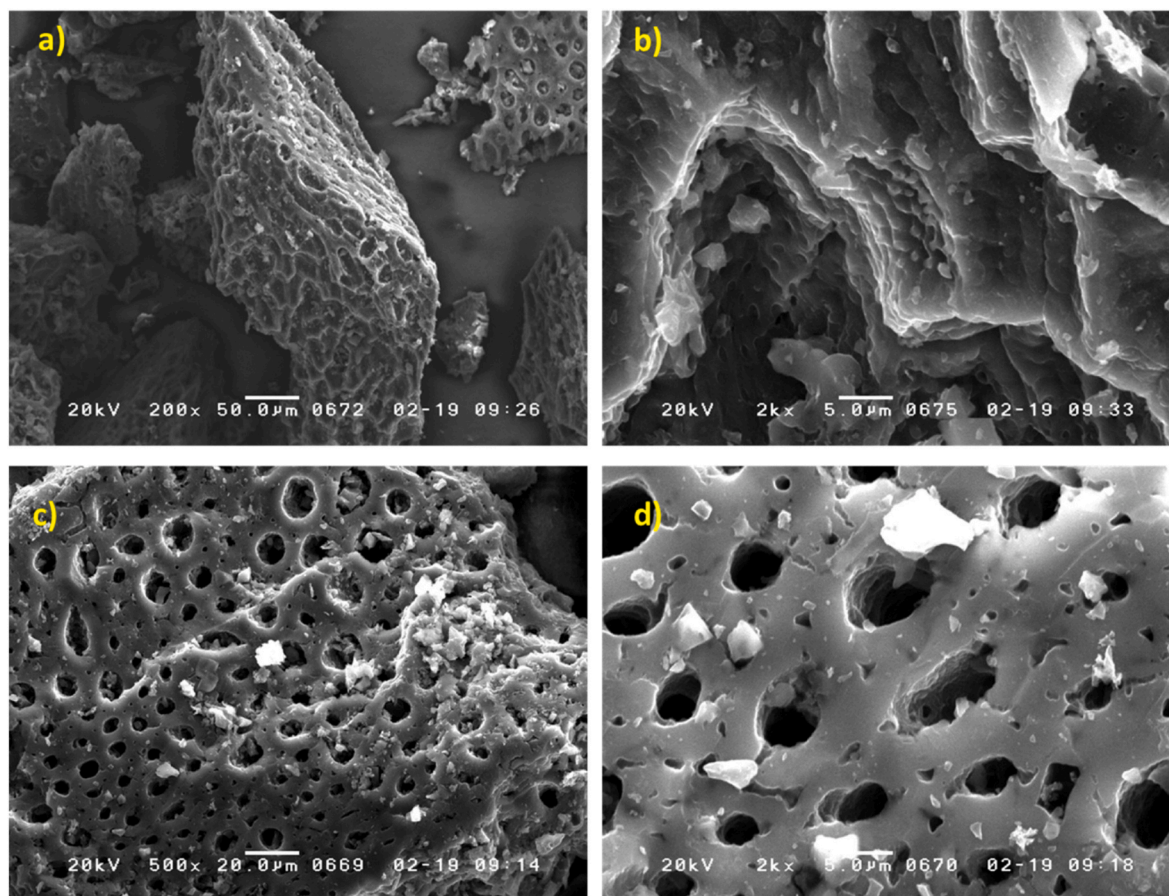


Fig. 3. SEM images of WpOH (a, b) and AsPhA (c, d) at different magnifications.

when AsPhA is negatively charged and the BTAs (except BTZ) are positively charged. Since the BTZ pK_a values are 1.6 and 8.9 (Table S1 and Fig. S5), BTZ was likely present as a neutral molecule in this pH range (pH 4–7). Given that adsorption occurred across the whole pH range (except at very alkali conditions (Figs. S2a–b)), electrostatic interactions were not solely responsible, and other non-pH-dependent mechanisms were involved in the overall adsorption process. Deng et al. (2019a, 2019b) reported similar results (with a sorbent pH_{pzc} of 2.4), wherein efficiency of BTA removal was highest at pH 4–8. At lower pH values, due to the positive charge of the adsorbent and protonation of the BTA molecules, it is not possible to achieve electrostatic interaction. At higher pH values, repulsion occurs between the negative charge of the adsorbent and the BTA molecules.

From the modelling here, the Elovich model fit could suggest that adsorption of BTAs was heterogeneous across the WpOH and AsPhA surfaces (Yu et al., 2022). Xu et al. (2010) showed similar results during adsorption of BTZ onto a Zn–Al–O binary metal oxide adsorbent, wherein the Elovich model had the highest correlation with the experimental data, which indicated that adsorption occurred across a heterogeneous surface. However, the best fit Freundlich isotherm (here) assumes an uneven distribution of active adsorption sites, across a heterogeneous surface, without saturation (Tran, 2020). Similar results were reported by Yu et al. (2022), wherein the authors hypothesised that the main reason for a high correlation between the Freundlich isotherm and the experimental data may be the existence of pores or wrinkles on the rough surface (of a polyvinyl chloride microplastic), which then caused uneven distribution of active adsorption sites. A similar scenario may apply here.

In terms of other mechanisms at play here, WpOH and AsPhA are hydrophobic materials due to their methyl, ethyl, alkyl, and aromatic

functional groups. Additionally, the BTA molecules all possess an aromatic benzene ring and a five-membered ring with nitrogen atoms. Therefore, hydrophobic interactions may well form between the hydrophobic surfaces of the biochar and the aromatic rings of the BTAs. Other studies, i.e., from Sarker et al. (2017) and Minh and Lee (2018), showed that this interaction could play an important role in the removal of BTAs onto carbonaceous materials.

Our FTIR and XPS analysis (Fig. 4a–f) also showed the contribution of H-bonding to the overall adsorption process. Fig. 4b suggested slight changes in C–O, P–O and O–H groups post-adsorption which could relate to bonds between hydroxyl groups (H-donors) on the biochar surfaces and oxygen and nitrogen (H-acceptors) on the BTAs (through dipole-dipole H-bonding). Another type of H-bond (i.e., Yoshida) could also occur between the biochar C–O, P–O and O–H groups and the aromatic BTA rings. Moreover, the peak intensity at binding energies of 530.78 eV and 532.68 eV (on Fig. 4e) decreased significantly due to the reaction between O=C=O and C–O plus P–O, respectively, with BTAs through H-bonding interactions. Fig. 4f showed that the intensity of nitrogen related peaks (i.e., $-NH_2$, etc.) increased, which could be explained, that these N related functional groups were likely involved in adsorption, forming H-bonds with N-containing BTA molecules. Similar results were also reported previously (Azzam et al., 2022; Deng et al., 2019a; Nguyen et al., 2020; Wang et al., 2017).

In terms of electron donor acceptor (EDA) bonds, we noted possible $n-\pi$ and $\pi-\pi$ EDA interactions. The $n-\pi$ EDA interactions could be described as bonds between carbonyl oxygen on biochar surfaces (as electron donors) and aromatic BTA rings (as electron acceptors). Here, XPS analysis (Fig. 4e) indicated changes in carbonyl oxygen (C=O) groups on the WpOH and AsPhA surface, which suggest the involvement of these functional groups with BTA aromatic rings (Nguyen et al.,

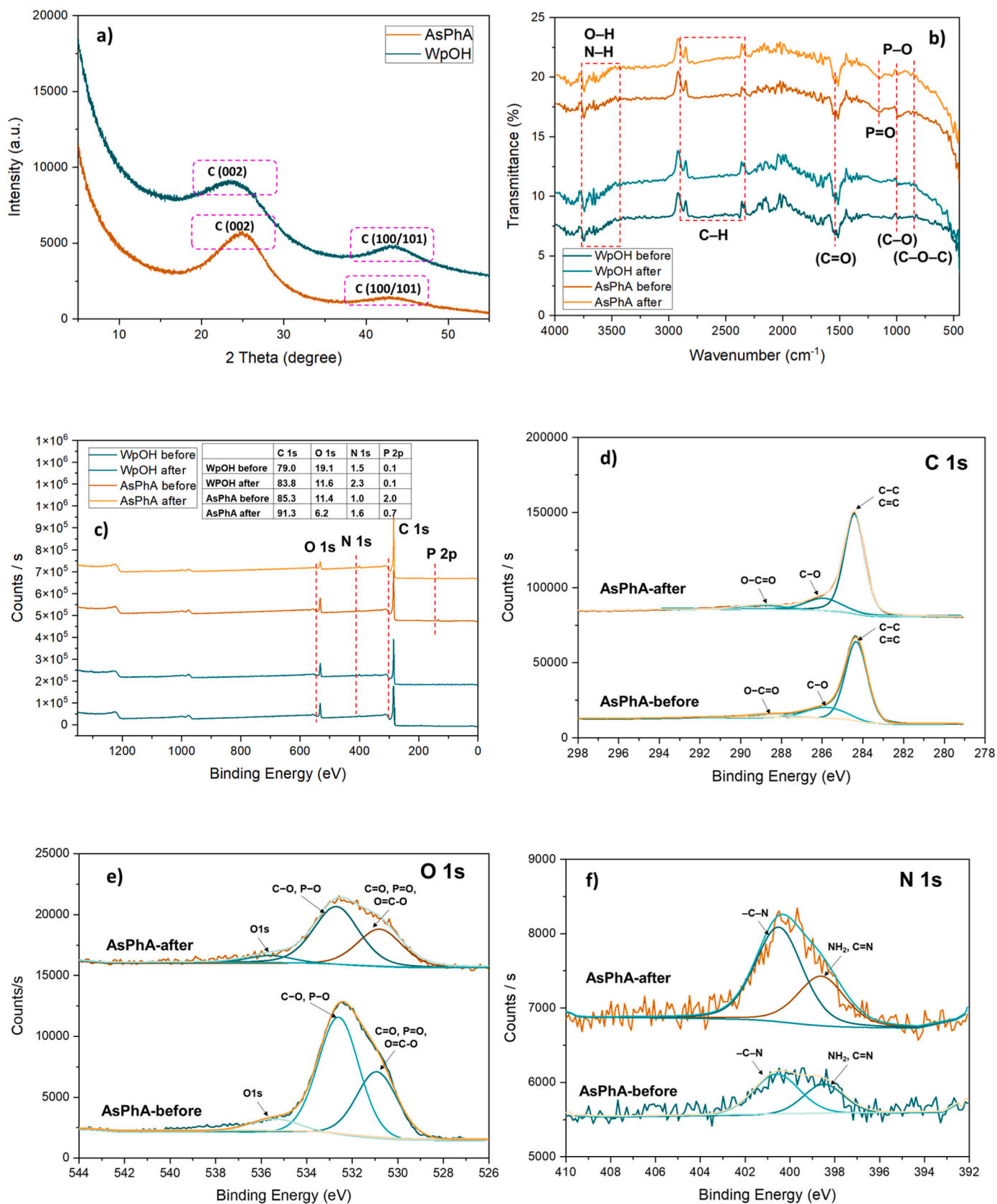


Fig. 4. XRD patterns (a), FTIR spectra (b) and XPS wide scan spectra (c) before and after adsorption for both biochars. XPS high resolution spectra of C 1s (d), O 1s (e) and N 1s (f) for AsPhA before and after adsorption.

Table 4

Deconvolution results for XPS spectra of WpOH and AsPhA before and after BTA adsorption.

Region	Assignments	WpOH		AsPhA	
		Before	After	Before	After
C1s	C–C	62.8	68.0	61.8	68.2
	C–O	11.9	12.4	12.2	13.5
	O–C=O	2.2	3.9	4.7	8.0
N1s	NH ₂ , C=N	0.6	0.8	0.5	0.8
	–C–N	0.6	2.2	0.7	1.6
O1s	C=O and P=O	12.7	5.3	7.3	2.5
	C–O and P–O	8.4	6.8	9.7	3.9
	O1s	1.0	0.4	1.0	0.5
P2p	Phosphates and pyrophosphates	0.1	–	2.1	0.8

2020). Additionally, the notable decrease in peak intensity (in FTIR spectra) after AsPhA saturation (Fig. 4b) related to phosphate and pyrophosphate groups, suggested that these functionalities also played a part in n- π EDA interactions (Pap et al., 2021b). Another contributor was π - π EDA interactions - that occurred between the π -electrons (donor) of the WpOH and AsPhA and the π -electrons (acceptor) in the BTA aromatic rings. Fig. 4d shows the XPS spectra of C1s, which showed that the carbon related functional groups on the biochars may be either aliphatic or aromatic, which is favourable for bonding to the BTA molecules via π - π EDA interactions (Keerthanan et al., 2020). Also, the peak at 284.38 eV (representing the C=C of aromatic C), showed an intensity increase and shift to 284.72 eV, after BTA adsorption. This may be due to the sp² C of aromatic C=C on the biochars with a partial positive charge and low electron density which can act as an electron donor during the adsorption process (Azzam et al., 2022). This may also explain the shift in other carbon-related peaks. This data supports the presence of π - π interactions between the biochars and BTAs (Azzam et al., 2022; Ninh et al., 2023). Q. Wu et al. (2022) also reported similar findings when working on sludge based biochars and fluoroquinolone (antibiotic) removal, wherein π - π interactions played a key role in adsorption. Feng et al. (2022) further showed that shifts in oxygen-containing functional

groups (in XPS spectra) indicated H-bonding with the hydroxyl, amino, and nitro groups of organic molecules.

Beside these interactions, pore filling and pore blocking will occur with micro- and macro-porous biochars. The diffusion of organic molecules (here BTAs) into the porous structure of a biochar (macro $\rightarrow$ meso $\rightarrow$ micro pores) is known as pore filling, but when the molecules being adsorbed are larger than the pore diameter, pore blocking will occur (Wang et al., 2022). Data from Table S1 and Table S4 show that the S_{BET}, micro- and total pore volumes of both biochars significantly decreased after BTA adsorption, suggesting that both pore filling and blocking were occurring at the liquid/solid interface.

In summary, the extensive instrumental characterisation and modelling data here suggest that pore filling through diffusion, with subsequent EDA interactions and H-bonding, were the governing mechanisms for BTA adsorption (Fig. 5). Electrostatic interactions were likely less important mechanisms.

When it comes to adsorption capacity, the maximum adsorption capacity for BTAs here is in line with other studies. The cumulative adsorption capacity (with a mixture of all 6 BTAs) was 379 mg/g for WpOH and 526 mg/g for AsPhA (see Table S5). It should be noted however that a direct comparison between $q_{\max}$ (mg/g) is only indicative because of the varying experimental conditions used across different studies.

For desorption, Tang et al. (2023) also showed that NaOH was the most suitable solution for regenerating biochar. Additionally, similar results were shown by Jiang et al. (2013), wherein BTZ and 5-tolyltriazole were examined alongside a novel MOF adsorbent. Therein, the most efficient desorption potential was obtained when applying NaOH/methanol (10:90, v/v). One possible explanation for the low desorption potential observed for both biochars with some solutions, more notably with WpOH, was the adsorption mechanisms involved here. If weak van der Waals forces and n- π EDA interactions were the governing adsorption mechanisms, higher BTA desorption could perhaps be achieved (Tomul et al., 2021). Another possible explanation is degradation capacity, i.e., biochars can have catalytic properties due to their large catalytic surface area and the abundance of active sites (Chen et al.,

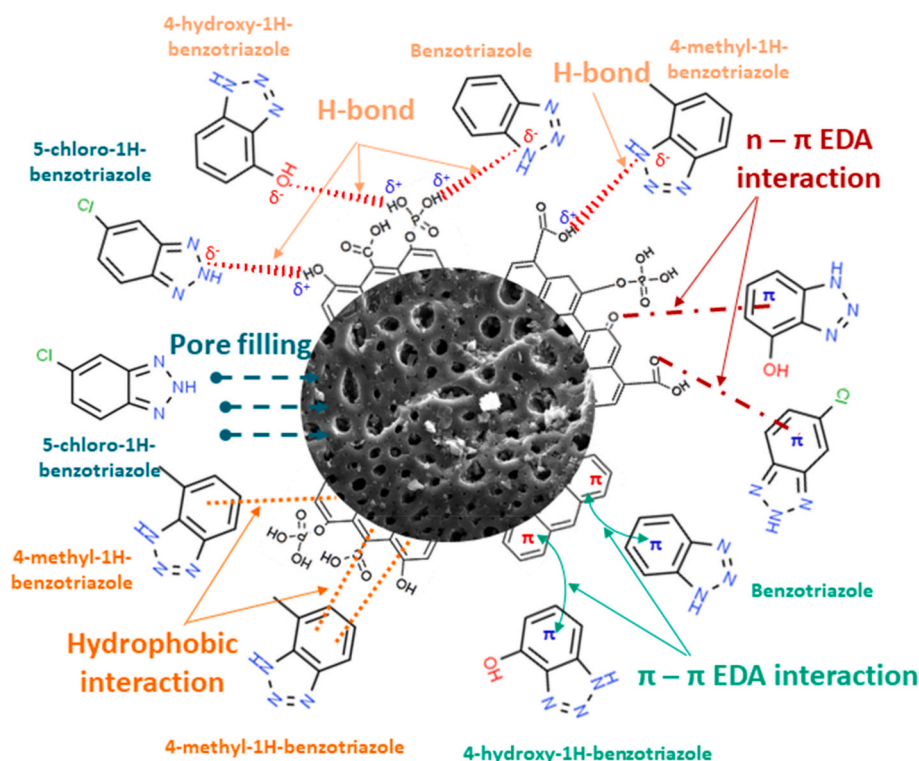


Fig. 5. Schematic of proposed key adsorption mechanisms for BTAs onto biochars.

2023). It could therefore be hypothesised that these functionalised biochars could degrade BTAs to a certain extent, which then renders the BTAs undetectable in the desorption eluent (Ma et al., 2022).

Wastewater usually contains low concentrations of BTAs ($\mu\text{g/L}$ or ng/L), as well as many other compounds which may affect the wastewater treatment process (Kraševac and Prosen, 2021). The results here showed that the investigated biochars were effective at these low concentration levels, which shows that they could be successfully implemented within existing WWTPs. It is however well recognised that matrix-related factors such as pH variation, presence of other ions, presence of humic/fulvic acids (i.e., high BOD and COD) and suspended solids may all significantly affect the performance of any adsorption process. Therefore, the implementation of these biochars would make most sense only as a final polishing step for BTA removal at a WWTP. Additionally, wastewater relative toxicity is a very important parameter and this study shows that biochar, most notably AsPhA, was effective at reducing the overall toxicity profile of the wastewater - and thus the risk to a recipient ecosystem. WpOH showed limited benefit in this regard. This could be related to the higher catalytic activity of WpOH and thus the potential formation of degradation by-products (Gvoic et al., 2022).

5. Conclusion

The effectiveness of the removal of these BTAs onto two lignocellulosic biochars, obtained from apricot (AsPhA) and wild plum (WpOH) stones was investigated. Two potential applications emerge from this work. First, it provides new insights and evidence regarding the adsorption mechanisms at play for BTAs and their adsorption onto these (and other similar) biochars. Second, this research showed that even at low, environmentally relevant concentrations, the biochars reduced BTA levels in real wastewater samples. As such, as lignocellulosic waste biomass is a globally abundant resource, it could provide a more cost effective and sustainable water treatment solution. However, it remains necessary to continue research in this area regarding removal of other emerging pollutants, and regarding real-world pilot-scale implementation at WWTPs. This may then lead to future practical applications for biochar within the wastewater treatment sector.

CRediT authorship contribution statement

Sabolc Pap: Conceptualization, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing, Funding acquisition, Project administration, Supervision. **Olivera Paunovic:** Investigation, Formal analysis, Visualization, Writing – original draft. **Helena Prosen:** Methodology, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Ida Kraševac:** Methodology, Validation, Data curation. **Polonca Trebše:** Conceptualization, Methodology, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Lydia Niemi:** Writing – review & editing. **Mark A. Taggart:** Writing – review & editing. **Maja Turk Sekulic:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.122205>.

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