



# Study of Adsorption Efficiency of Lignite, Biochar, and Polymeric Nanofibers for Veterinary Drugs in WWTP Effluent Water

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**Abstract** The increased consumption, overuse, and subsequent difficult removal of pharmaceuticals using conventional processes lead to their rising prevalence in the environment. Adsorption belongs to the most efficient approaches to pharmaceuticals' removal from wastewater. This study provides insight into the sorption properties of biochar, lignite, and polyamide nanofibers (PA-nanofibers) for sulfamethoxazole, trimethoprim, clarithromycin, azithromycin, and amoxicillin in ultrapure and wastewater treatment

plant (WWTP) effluent water. The negative effect of WWTP effluent water was reflected in a reduction of the sorption capacity of biochar by 6.31–72.15%, 25.58–98.55% for lignite, and 4.21–67.71% for PA-nanofibers. Simultaneously, this study investigates the impact of the experimental setup. The sorption capacities were recorded in the range from 0.65 to 2.84 mg g<sup>-1</sup> for biochar, 0.04 to 75.73 µg·g<sup>-1</sup> for lignite, and 0.53 to 30.54 µg·g<sup>-1</sup> for PA-nanofibers during the fixed-bed column tests with WWTP effluent water. Based on the results, biochar appears to be a suitable sorbent for selected pharmaceuticals in field conditions with running water. Lignite and PA represent complementary treatment technology or can act as a carrier for microbial degraders. Performed batch tests with ultrapure and WWTP effluent water and subsequent column tests highlighted the importance of conducting tests with the appropriate matrix and experimental setup to gain a realistic insight into the behavior of the sorbents under environmentally relevant conditions.

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## 1 Introduction

Veterinary pharmaceuticals (VPs) are widely used for animals' prophylaxis and treatment of infectious diseases (Dolliver et al., 2008; McGregor et al., 2007).

Together with other compounds like pesticides, personal care products, industrial substances, and drugs (and their metabolites) belong to the group of micropollutants. Micropollutants (MP) can be of anthropogenic or natural origin, and they are found in the water environment at very low concentrations (from  $\text{ng}\cdot\text{L}^{-1}$  to  $\mu\text{g}\cdot\text{L}^{-1}$ ) (Bimová et al., 2021; Clara et al., 2005; Ribeiro et al., 2015). The presence of micropollutants in the environment could adversely affect aquatic organisms and human health. Besides that, they have been associated with the endocrine-disrupting effect. Elevated concentrations of antibiotics in the environment could also lead to the selective proliferation of resistant bacterial strains (Aguilar-Pérez et al., 2020; Bair et al., 2016; Luo et al., 2014; Ribeiro et al., 2015). The major causes of their occurrence are high consumption, misuse, and wastewater treatment plants (WWTPs), which have limited efficiency in removing the compounds mentioned above (Camiré et al., 2020; Kurwadkar et al., 2015; Ribeiro et al., 2015). Conventional WWTPs are based on physical (sedimentation, adsorption, membrane filtration) and biological methods (transformation and biodegradation) as well as their combinations (Dalahmeh et al., 2018; Kebede et al., 2020; Rostvall et al., 2018; Shin et al., 2021). As additional treatment steps, physicochemical processes such as advanced chemical oxidation or sorption units are considered today. Adsorption is one of the most used approaches in the case of the removal of pharmaceuticals from WWTP effluent water. Some authors claim easiness of operation (Shin et al., 2021), cost-efficiency, and simplicity of adsorption treatment steps (Kebede et al., 2020). However, surface active compounds of microbial and artificial origin are present in wastewater making it one of the most complex environmental matrixes. Under such conditions, efficient employment of adsorption processes is rather uneasy and complicated. The adsorption efficiency is influenced by the physicochemical properties of pollutants, interactions between the targeted compounds and the matrix, properties of the WWTP effluent water, and used sorbents (Kebede et al., 2020; Rostvall et al., 2018). Therefore, the selection of a suitable sorbent for a specific application has been the subject of many researches during the last few years.

Biochar is a material with a high percentage of carbon, a byproduct created by the heating of organic waste under absolute or partial oxygen deficiency. Biochar is characterized by a large hydrophobic

surface area with a high-density negative charge, a high number of functional groups, stability and a low cost of its production (Bair et al., 2016; Lehmann and Joseph, 2015; Ren et al., 2020; Shin et al., 2021; Zhang et al., 2020). Based on these properties, biochar is suitable for the adsorption of selected compounds (Bair et al., 2016; Vinayagam et al., 2022). Numerous types of research have been published on the implementation of biochar as a sorbent for pharmaceuticals (Bimová et al., 2021; Clara et al., 2005; Dalahmeh et al., 2018; Shin et al., 2021; Yao et al., 2012), heavy metals (Bair et al., 2016; Komkiene and Baltreinaite, 2016; Samsuri et al., 2014), and dyes (Ahmad et al., 2020; Bordoloi et al., 2017; Dawood et al., 2019).

Lignite, the brown coal youngest type, contains numerous hydroxyl and carboxyl groups thanks to the humic substance, which are the primary reservoir of these functional groups (Havelcová et al., 2009). The presence of these oxygen-containing groups allows the adsorption of metal ions (Havelcová et al., 2009; Mohan and Chander, 2006), pharmaceuticals and other micropollutants (Redding et al., 2009; Rostvall et al., 2018), aromatic compounds, and petroleum contaminants (Aivalioti et al., 2012; Polat et al., 2006). Polat et al. (2006) point out that in the case of phenol adsorption, the lignite adsorption capacity ( $10 \text{ mg}\cdot\text{g}^{-1}$ ) was lower than the activated carbon adsorption capacity (around  $300 \text{ mg}\cdot\text{g}^{-1}$ ). However, after normalization for the surface area, lignite showed better adsorption results ( $1.3 \text{ mg}\cdot\text{m}^{-2}$ ) compared to carbon ( $0.05\text{--}0.3 \text{ mg}\cdot\text{m}^{-2}$ ). Further, the heat treatment of lignite can increase the surface area, which often translates to better adsorption properties (Aivalioti et al., 2012). Besides the activated carbon, lower price and easy availability make lignite a suitable alternative adsorption material without regeneration necessity and the possibility to use as a fuel for heat processing after its saturation (Aivalioti et al., 2012; Polat et al., 2006).

Polymeric nanofibers are the other promising material that could find application in WWTP effluent water treatment. They are, in most cases, produced by electrospinning from a polymer solution. The significant advantage of nanofibers is the high surface area-to-volume ratio, which is further enhanced by the high porosity of nanofibers. Along with the above, the possibility of surface modification can positively influence adsorption capacity and kinetics (Cui et al., 2020; Háková

et al., 2020). Similarly, to biochar and lignite, polymeric nanofibers have been used for removing different compounds from the environment. Camiré et al. (2020) used lignin with poly(vinyl) alcohol nanofibers for fluoxetine removal from the WWTP effluent water. Obtained nanofibers showed 70% efficiency in adsorbing fluoxetine after dual-stage stabilization. Another example of successful adsorption is the work of authors Abdmaleki et al. (2018) — their research was focused on the adsorption of tetracycline using the chitosan/PVA crosslinked with glutaraldehyde. The nanofibers from Moringa seeds protein/PVA were used to remove non-steroidal anti-inflammatory drugs and carbamazepine (Kebede et al., 2019). Polycaprolactam (Nylon 6) nanofibers and polyacrylonitrile nanofibers with and without ethanalamine modification could effectively adsorb dyes from aqueous media (Qureshi et al., 2017). A wide range of nanofibers can be used for the adsorption of metal ions (Choi et al., 2020; des Ligneris et al., 2020; Sehaqui et al., 2014; Ullah et al., 2020).

Our research is focused on the comparison of three very diverse materials — biochar, lignite, and polyamide-nanofibers (PA-nanofibers) as suitable candidates for the removal of the selected veterinary pharmaceuticals. These compounds have been chosen based on their high consumption in veterinary medicine in the Czech Republic (ÚSKVBL, 2019). Batch experiments were performed to determine the effect of the matrix on the parameters of the Langmuir and Freundlich isotherms. Finally, the column tests with pharmaceuticals in WWTP effluent water were used to obtain more realistic data regarding sorption onto selected sorbents. This research is not concerned with optimizing the conditions for obtaining the highest sorption efficiency but is focused on comparing the sorption capacities of given sorbents under certain conditions. The aim of this work is to show the degree of reduction in sorption capacity when different media, and experimental setups are used. Furthermore, there is an attempt to keep the design as simple as possible with a view to easy implementation at contaminated sites. To the best of our knowledge, there are no in-depth studies comparing the sorption capacities of selected pharmaceuticals by these sorbents obtained *via* similar experimental setups.

## 2 Materials and Methods

### 2.1 Chemicals and Solutions

Analytical standards of pharmaceuticals (sulfamethoxazole, SMX; trimethoprim, TMP; clarithromycin, CLA; and azithromycin dihydrate, AZM) for LC/MS development and optimization were purchased from Chromservis (Prague, CZE). Amoxicillin trihydrate (AMX) was purchased from Sigma-Aldrich (St. Louis, MO, USA). D4-Acetaminophen (HPC Standards GmbH, Borsdorf, GER) was used as an internal standard. The available pills were used for sorption tests to simulate real conditions — cotrimoxazole AL FORTE containing SMX and TMP (ALIUD PHARMA GmbH & CO.KG., Laichingen, GER), Sumamed with AZM content (PLIVA HRVATSKA d.o.o, Zagreb, HR), Klacid 500 containing CLA (Abbott Laboratories Ltd, Maidenhead, GB), and Duomox 1000 with AMX content (Astellas Pharma s.r.o., Prague, CZE). The stock solutions for all analytes were prepared by dissolution of pills in pure methanol to achieve a concentration of  $1 \text{ gL}^{-1}$  of active compounds. The stock solutions were placed in the ultrasonic bath for 15 min and filtrated through the glass fiber syringe filter with a pore size of  $0.22 \text{ }\mu\text{m}$  (Cobetter, Hangzhou, CHN). The obtained concentrations were verified by LC-MS/MS. Optima LC-MS grade methanol, and formic acid was purchased from Fisher Scientific (Pittsburgh, PA). Ultrapure water ( $18.2 \text{ M}\Omega\text{-cm}^{-1}$ , VWR Puranity TU+ Ultrapure water system, Gemini B.V. Apeldoorn, NL) and effluent from municipal WWTP (Liberec, CZE; GPS coordinates 50.7800914N, 15.0326631E; further information about WWTP is provided in Supplementary Material) were used for batch static tests. The WWTP effluent water of the given origin was used for kinetic column experiments.

### 2.2 Sorbent Characterization

The used biochar was purchased by the company Biouhel s.r.o. (Zlín, CZE). Biochar was prepared by pyrolysis of a mixture of waste biomass from agricultural harvests of annual and biennial plants and digestate from a biogas plant, mixed in a ratio of 60:40%. Pyrolysis of the biomass was carried out for 50 min

at a maximum temperature of 570 °C. The material was sieved to < 4 mm. Lignite was purchased by the company Baňa Čáry (Čáry, SK). For the analysis, a fraction of lignite < 2 mm was used. Composite PES yarns with a nanofibrous envelope from polyamide 4/6 (PA 4/6) have been chosen for this experiment. The composite nanofibers yarns were purchased from the company Nanoprogress (Liberec, CZE). The density of the nanofibers was 600 dtex.

### 2.2.1 Elemental Analysis of Sorbents

Elemental analysis of sorbents was performed using equipment Elementar Vario Cube with TCD detection (Elementar Analysensysteme GmbH, Langensfeld, GER). The module with a combustion tube temperature of 1150 °C and a reduction tube temperature of 850 °C was used. Acetanilide was used as an internal standard. A total of carbon ( $C_{\text{tot}}$ ), hydrogen, nitrogen, and sulfur (HNS) were determined with this method. Organic carbon ( $C_{\text{org}}$ ) was calculated as a difference between  $C_{\text{tot}}$  and inorganic C originating from the carbonates (Bachmann et al., 2016; Brunauer et al., 1938). The ash was determined *via* muffling at 700 °C. Oxygen content was calculated using the formula (Bimová et al., 2021):

$$O_{\text{tot}} = 100 - (C_{\text{tot}} + H + N + S + \text{ash}) \quad (1)$$

### 2.2.2 Brunauer-Emmett-Teller Analysis of Sorbents

The nitrogen/krypton adsorption method and Brunauer-Emmett-Teller (BET) adsorption isotherm were used to determine the specific surface areas of the sorbents using gas sorption analyzer Autosorb iQ MP and ASiQwin software (Quantachrome, USA). All samples were degassed under a vacuum prior to the measurements. The BET specific surface areas were calculated from the volume of gas adsorbed (nitrogen or krypton) at relative pressures between 0.05 and 0.30, where the BET isotherm was linear.

### 2.2.3 Image Analysis by Scanning Electron Microscope

The morphology of the PA 4/6 nanofibers was analyzed using a TESCAN Vega 3 (Brno, CZE)

scanning electron microscope. The samples for analysis were coated (*via* sputtering) with 7 nm of gold (Quorum SC7620, UK) to minimize the charging effects prior to viewing. The fiber diameters were determined using Fiji ImageJ (National Institutes of Health, MD, USA) software (ver. 2.3.0.) by measuring 100 randomly observed fibers on images acquired at a magnification of 5000×.

### 2.3 LC-MS/MS Analysis Setup

LC-MS/MS system was used for the determination of VPs. The analysis was performed on an ExionLC system (AB Sciex, Framingham, USA) equipped with QTOF X500R with electrospray ionization (ESI) Turbo V ion spray (AB Sciex, Framingham, USA). The Triart C18 column (100 mm × 2.1 mm I. D., 3 μm, YMC CO., LTD., Kyoto, JP) was used to separate analytes. The mobile phase consisted of a binary gradient of 0.1% formic acid (phase A) and methanol (phase B). The flow was set at 0.42 μL min<sup>-1</sup>, the column compartment temperature was 40 °C, and the injection volume was 20 μL. The analysis lasted 16.2 min. Quantifying of pharmaceuticals was performed in positive mode using schedule multiple reaction monitoring (sMRM). ESI<sup>+</sup> settings were temperature of 550 °C and spray voltage of 5500 V. The curtain gas and collision gas (CAD) were set at 35 and 7 psi, respectively. Ion source gas 1 and 2 were set at 30 and 40 psi, respectively. Collision energy (CE) and declustering potential (DP) were optimized for each of the selected compounds.

### 2.4 Experimental Setup

#### 2.4.1 Adsorption Experiments

To measure the maximum adsorption capacity and matrix impact assessment, the batch static tests were carried out. For the batch test, 50 mg of each sorbent and 30 ml of individual pharmaceuticals at different concentrations in ultrapure water or WWTP effluent water were used. The reaction conditions were as follows: shaking at 150 rpm, temperature ± 21 °C, and reaction time of 1 h. The obtained data were evaluated with the Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm is expressed by

Eq. (2); the Freundlich isotherm is described by Eq. (3) (Foo and Hameed, 2010; Li et al., 2018).

$$C_e/q_e = 1/q_m k_l + C_e/q_m \quad (2)$$

$$q_e = K_f \cdot C_e^{1/n} \quad (3)$$

where  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ,  $\mu\text{g}\cdot\text{L}^{-1}$ ) and  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ,  $\mu\text{g}\cdot\text{g}^{-1}$ ) are the concentrations of pharmaceuticals in solution and in the adsorbent at the equilibrium,  $k_l$  is the Langmuir constant,  $q_{m,u}$  ( $\text{mg}\cdot\text{g}^{-1}$ ,  $\mu\text{g}\cdot\text{g}^{-1}$ ) represents the maximum adsorption capacity in the ultrapure water;  $q_{m,w}$  ( $\text{mg}\cdot\text{g}^{-1}$ ,  $\mu\text{g}\cdot\text{g}^{-1}$ ) is the maximum sorption capacity in WWTP effluent water;  $K_f$  and  $n$  are the parameters related to the adsorption process and describing of the adsorbents surface properties (Bimová et al., 2021; Jung et al., 2013; Li et al., 2018). In general, a high value of  $K_f$  is indicative of favorable adsorption processes, while the reciprocal of  $n$  has a meaning of surface heterogeneity (homogeneous surface;  $n = 1$ ) (Jung et al., 2013).

#### 2.4.2 Column Experiments

The fixed-bed column experiments were carried out to create the breakthrough curves for each sorbent and veterinary pharmaceuticals in WWTP effluent water. The miniature glass columns with dimensions of 8.8 cm in length and an internal diameter of 0.4 cm were used. The concentrations of target VP were set according to the  $q_{m,w}$  from the isotherm measurements to achieve 50% of inlet concentration within one hour. The solutions were delivered using the PVC tubes and peristaltic pump NK M PRO2 (Injecta S.r.l., IT) with the flow rate of  $1 \text{ ml}\cdot\text{min}^{-1}$ . Column tests were performed at constant temperature of  $\pm 22$  °C. Reaction time was 80 min, and the samples were taken regularly. The collection time was 1 min. The adsorbed amount of VP was calculated from Eq. (3) (García-Sánchez et al., 2014; Taty-Costodes et al., 2005).

$$q_{50} = (Q_v \cdot t_{50} \cdot C_0) / m_c \quad (4)$$

where  $q_{50}$  ( $\text{mg}\cdot\text{g}^{-1}$ ;  $\mu\text{g}\cdot\text{g}^{-1}$ ) is the adsorption capacity of sorbents in the column at 50% of inlet concentration;  $Q_v$  represents flow rate effluent ( $\text{L}\cdot\text{min}^{-1}$ );  $t_{50}$  (min) is the time when the outlet concentration

reaches 50% of the inlet concentration  $C_0$  ( $\text{mg}\cdot\text{L}^{-1}$ ;  $\mu\text{g}\cdot\text{L}^{-1}$ );  $m_c$  (g) is the adsorbent mass (García-Sánchez et al., 2014; Taty-Costodes et al., 2005). For the analysis, 1 ml of all water samples were taken and filtrated through the glass fiber syringe filter with a pore size of  $0.22 \mu\text{m}$  (Cobetter, Hangzhou, CHN). The filtrated sample was placed into 2-ml vials, and the internal standard was added. All samples prepared in this way were stored in the fridge (4 °C) prior to the LC/MS/MS analysis.

### 3 Results and Discussion

#### 3.1 Results of Sorbents Characterization

##### 3.1.1 Results of Elemental Compositions and BET Analysis

The results of the elemental composition and BET analysis are listed in Table 1. The content of  $C_{\text{org}}$  was the highest in the biochar samples. According to International Biochar Initiative (2015), used biochar could be included into the first class due to the  $C_{\text{org}}$  content above 60%. If the  $C_{\text{org}}$  content is 30–60%, then it is second-class biochar, and third-class biochar contains at least 10% carbon. The second most abundant element is oxygen. In the case of biochar, the molar H/ $C_{\text{org}}$  and O/ $C_{\text{org}}$  ratios are used for the material stability description. The H/ $C_{\text{org}}$  value is 0.02. This value does not exceed the upper limit of 0.7 to consider biochar a stable material (International Biochar Initiative, 2015). The O/ $C_{\text{org}}$  value is 0.45. This result suggests classifying the used biochar as the intermediate half-lives (100–1000 years) material (Spokas, 2010). Lignite and nanofibers had lower content of carbon but a higher percentage of other elements; however, in contrary to biochar, sulfur was detected in both these materials. The molar H/ $C_{\text{org}}$  and O/ $C_{\text{org}}$  ratios were calculated for nanofibers and lignite to be 0.12 and 0.98, and 0.10 and 0.51, for lignite and nanofibers, respectively. The surface area of all materials was determined according to the BET theory. All samples were degassed prior to analysis at different temperatures — biochar (300 °C; 5 h), lignite (300 °C; 72 h), and PA-nanofibers (45 °C; 72 h). The volumes of adsorbed gas (nitrogen for biochar and nanofibers; krypton for lignite) were used to calculate the BET surface areas.



### 3.1.2 Characterization of the Adsorbents' Morphology

Scanning electron microscopy (SEM) images of all the tested sorbents before the sorption tests are depicted in Fig. 1. SEM images show that the sorbents differed markedly in surface structure. It can be seen from Fig. 1A that biochar had a complex microstructure comprised of heterogeneous pores of different scales and shapes. The surface of biochar was formed mainly by honeycomb-like openings densely covered with particles of irregular shape and size. Images of the microstructure of lignite (Fig. 1B) reveal bundles of heterogeneous particles attached to a smooth surface with rare cracks. The nanofibrous envelope of PA 4/6 (Fig. 1C) exhibited a dense and relatively homogeneous structure of beadless nanofibers. The PA 4/6 fibers had a relatively narrow fiber diameter distribution, with the mean fiber diameter measured to be  $236 \pm 105$  nm ( $n=100$ ).

### 3.2 LC/MS/MS Analysis

The selected pharmaceuticals were determined using LC/MS/MS. The stock solutions were prepared at

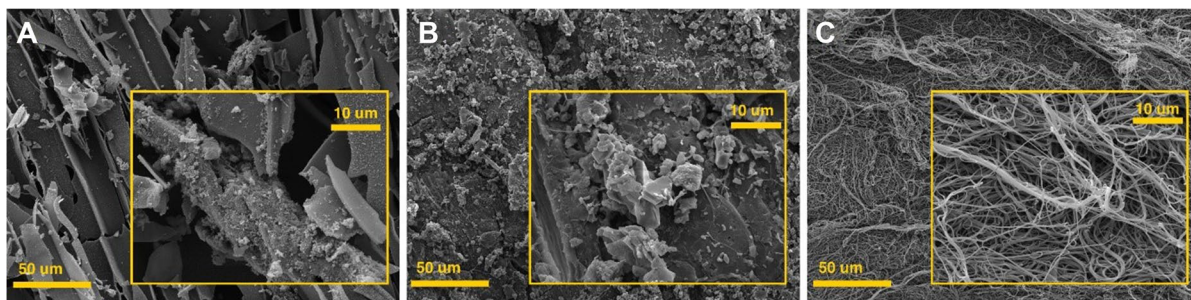
the concentration of  $1 \text{ g}\cdot\text{L}^{-1}$  in methanol for all analytes. The optimization and calibration solutions were prepared by diluting of standard solution. The MRM transition, CE and DP were optimized for all analytes. The MRM transition, linear range, limits of detection (LOD), and quantification (LOQ) are listed in Table S1 in the Supplementary Material. LOD and LOQ were calculated as signal-to-noise ratios of 3 and 10, respectively.

### 3.3 Results of the Sorption Batch Tests

The influence of the used matrix was evaluated *via* batch test for individual sorbent and pharmaceutical in ultrapure water and as well as in WWTP effluent water. The obtained graphs are shown in Fig. 2 and Fig. 3. For better clarity of the graphs, either the Freundlich or Langmuir isotherm was chosen for the graphs based on the value of the determination coefficients ( $R^2$ ). The Langmuir empirical model is based on the assumed monolayer adsorption at the fixed number of identical and equivalent sites (Foo and Hameed, 2010). The Freundlich isotherm is the model describing the reversible and non-ideal adsorption at the heterogenous surface with the non-uniform

**Table 1** Elemental compositions and BET results for examined sorbents

Sorbent	$C_{\text{tot}}$	$C_{\text{org}}$	H	N	S	Ash	O	Specific surface area
	%	%	%	%	%	%	%	$\text{m}^2\cdot\text{g}^{-1}$
Biochar	66.81	65.61	1.34	0.25	Not detected	1.79	29.81	368.80
Lignite	43.63	42.85	4.93	0.47	1.19	7.79	41.99	0.17
PA 4/6	59.67	58.60	5.67	4.24	0.32	0.26	29.84	4.00



**Fig. 1** Scanning electron microscopy (SEM) images of tested sorbents before the sorption experiment — biochar (A), lignite (B), and PA 4/6 (C). The scale bar on the right is  $10 \mu\text{m}$ , the scale bar on the left is  $50 \mu\text{m}$

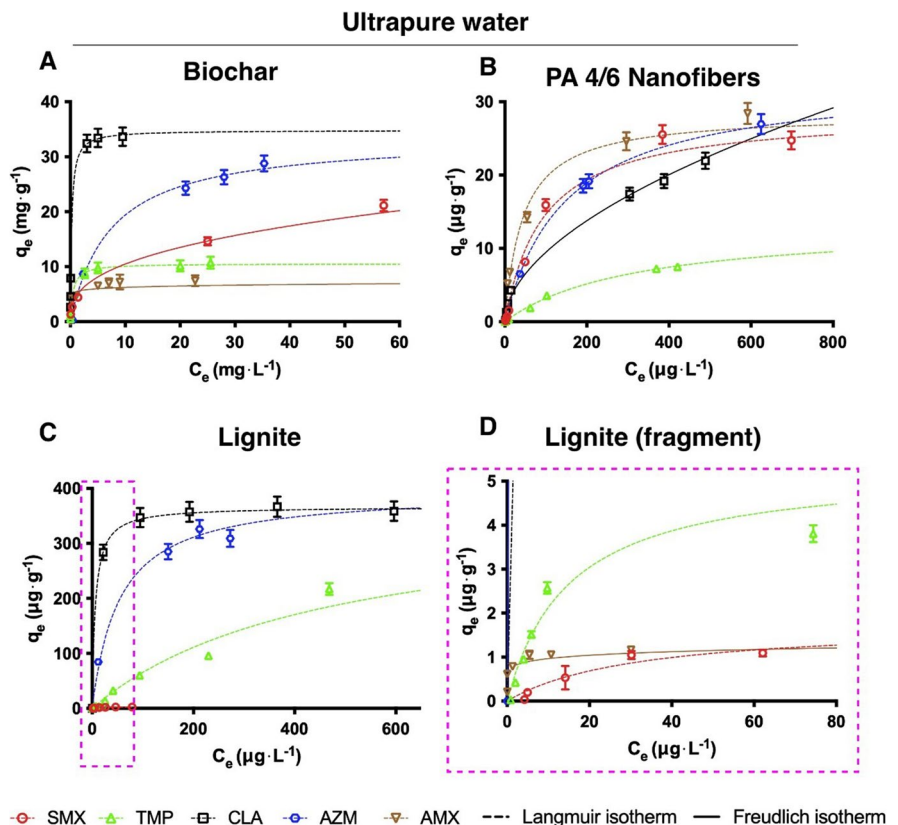
distribution of the adsorption affinity (Foo and Hameed, 2010; Li et al., 2018). All fitting parameters are listed in Table S2 in Supplementary Material.

Biochar showed the highest  $q_{m,u}$  for the VP in the order of tens of  $\text{mg}\cdot\text{g}^{-1}$ . The  $q_{m,u}$  decreases in the order — CLA ( $34.92 \text{ mg}\cdot\text{g}^{-1}$ ) > AZM ( $34.80 \text{ mg}\cdot\text{g}^{-1}$ ) > SMX ( $26.39 \text{ mg}\cdot\text{g}^{-1}$ ) > TMP ( $10.25 \text{ mg}\cdot\text{g}^{-1}$ ) > AMX ( $7.84 \text{ mg}\cdot\text{g}^{-1}$ ). When WWTP effluent water was used as the medium, the  $q_{m,w}$  decreased by 6.31–72.15 % depending on the VP (specific values are given in Table S2 in Supplementary Material). The high sorption activity can be justified by the large specific surface area determined by the BET analysis, which reaches a value of  $368.80 \text{ m}^2\cdot\text{g}^{-1}$ . According to the literature, biochar is abundantly used for pharmaceutical remediation. The adsorption capacity depends on many factors—adsorbate type and its physicochemical properties, the source of the biochar, the production process, and surface modification. These factors influence the biochar properties as the specific surface area, pore size, and surface functional groups (Ihsanullah et al., 2022; Monisha

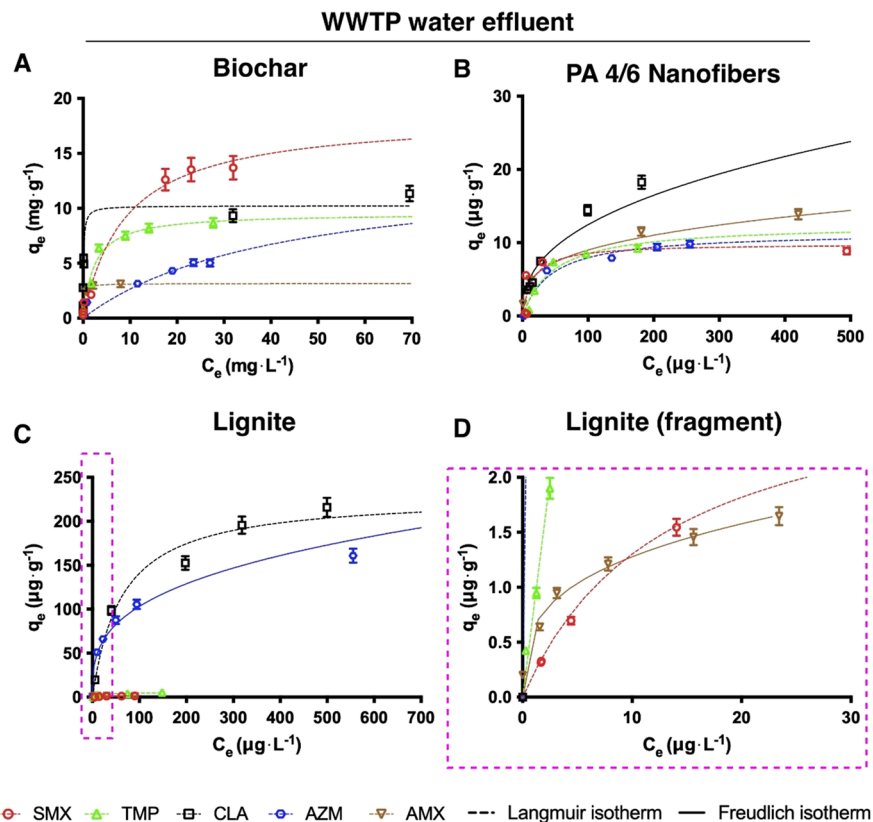
et al., 2022). However, many studies conducted batch experiments in pure water (Czech et al., 2021; Geng et al., 2021; Meng et al., 2020; Singh et al., 2021), without considering the negative impact of ballast substances in WWTP effluent. Similar research was carried out by Huang et al. (2020), who compared the difference in sorption capacities of biochar for SMX and sulfapyridine (SPY) using pure and WWTP effluent as the matrixes. In the case of SMX, the authors observed a significant decrease in the maximum sorption capacity when using wastewater as a medium ( $q_{m,u} = 100.30 \text{ mg}\cdot\text{g}^{-1}$ ;  $q_{m,w} = 24.30 \text{ mg}\cdot\text{g}^{-1}$ ). The authors attribute this decrease mainly to the presence of matrix ballasts competing for binding to biochar and pH, which affects the electrostatic interaction between SMX and biochar.

With respect to the detected specific surface area of lignite and nanofibers, the maximum sorption capacity was in the order of  $\text{ug}\cdot\text{g}^{-1}$ . In the case of lignite, the  $q_{m,u}$  were highest for AZM ( $394.56 \text{ ug}\cdot\text{g}^{-1}$ ), CLA ( $368.92 \text{ ug}\cdot\text{g}^{-1}$ ) and TMP ( $367.21 \text{ ug}\cdot\text{g}^{-1}$ ) then for SMX ( $1.79 \text{ ug}\cdot\text{g}^{-1}$ ) and AMX ( $1.03 \text{ ug}\cdot\text{g}^{-1}$ ). The lower

**Fig. 2** Adsorption isotherms for given sorbents and compounds in the ultrapure water - biochar (A), PA 4/6 (B), lignite full range (C) and fragment for low concentration range (D)



**Fig. 3** Adsorption isotherms for given sorbents and compounds in the WWTP water effluent - biochar (A), PA 4/6 (B), lignite full range (C) and fragment for low concentration range (D)



$q_{m,u}$  for lignite, compared to biochar, could be caused by several reasons. The first reason is the specific surface area. For the lignite we used, this value was determined at  $0.17 \text{ m}^2 \cdot \text{g}^{-1}$ , approximately 2 170 times less than that for biochar. In the literature, the values were higher —  $4.17 \text{ m}^2 \cdot \text{g}^{-1}$  (Polat et al., 2006), 2.06, 2.96, and  $2.20 \text{ m}^2 \cdot \text{g}^{-1}$  (Pehlivan and Arslan, 2006),  $5.3 \text{ m}^2 \cdot \text{g}^{-1}$  (Rostvall et al., 2018). The lignite-activated coke study by Wu et al. (2020) showed the BET value of  $224 \text{ m}^2 \cdot \text{g}^{-1}$ . The sorbent treatment before use is also a parameter affecting the sorption. Another reason may be the material's porosity (Wu et al., 2020). According to the SEM analysis, a smooth lignite surface with heterogeneous particles with no visible pores is evident, which may have an adverse effect on VP sorption. The high oxygen content is bound in the lignite structure in the form of hydroxyl and carboxyl groups. For this reason, it is often used for ion exchange (Jochová et al., 2004), especially in the case of heavy metal sorption, where pH is one of the crucial parameters. However, in this case, the most straightforward possible process without pH adjustment was investigated for simpler implementation of the method in practice. Last but not

least, sorption is affected by the organic matter background of the matrix. In the case of WWTP effluents, both organic compounds are present: (i) sorbates competing for the sorption places and (ii) surface active compounds that influence desorption processes *via* water surface tension modification. The effect of the WWTP effluent water matrix caused a decrease of 25.58–98.55 %. The physicochemical properties of VP can justify significant differences between VP sorption behavior. CLA and AZM are more lipophilic ( $K_{ow} = 3.16$  for CLA and 4.02 for AZM) (McFarland et al., 1997), whereas other examined compounds are considerably less lipophilic — SMX ( $K_{ow} = 0.89$ ) (Hansch et al., 1995), TMP ( $K_{ow} 0.91$ ) (Hansch et al., 1995), and AMX ( $K_{ow} = 0.87$ ) (Harrower et al., 2021). All of the above parameters should be considered when using lignite for sorption.

The specific surface area was determined to be  $4.00 \text{ m}^2 \cdot \text{g}^{-1}$  for PA4/6 nanofibers (approximately 90 times less than that for biochar). The  $q_m$  was influenced by the presence of the core yarn as the carrier. Nanofibers formed about 45% of the weight of used composite material. It can be hypothesized that using



the same amount of nanofibers alone would increase the adsorption capacity. However, this experiment is focused on the use of sorbent in practice, for example, at contaminated sites. Therefore, a commercially available product has been chosen, which can also be used as a suitable carrier for bacterial biomass, which may be involved in the chemical degradation of compounds (Nechanická et al., 2021). The  $q_{m,u}$  values found for tested VP were as follows SMX (30.54  $\mu\text{g}\cdot\text{g}^{-1}$ ), TMP (13.34  $\mu\text{g}\cdot\text{g}^{-1}$ ), CLA (60  $\mu\text{g}\cdot\text{g}^{-1}$ ), AZM (33.08  $\mu\text{g}\cdot\text{g}^{-1}$ ), and AMX (29.72  $\mu\text{g}\cdot\text{g}^{-1}$ ). Compared to lignite, the differences between the VP were not so pronounced. However, this material was also adversely affected by ballast substances in the WWTP effluent water by 4.21–67.71%. Based on these values, on average, nanofibers were affected to the least extent compared to lignite and biochar. According to the published literature, electrospun nanofibers of protein from *Moringa stenopetala* seeds and polyvinyl alcohol were used for SMX sorption (Kebede et al., 2020). These nanofibers had a specific surface area of 2402.62  $\text{m}^2\cdot\text{g}^{-1}$  correlated positively with the Langmuir  $q_m$  of 166  $\text{mg}\cdot\text{g}^{-1}$ . In this case, there was no significant decrease in the adsorbed amount of SMX when these nanofibers were applied to real wastewater samples. The authors report the values of  $q_e = 41.35 \text{ mg}\cdot\text{g}^{-1}$  for deionized water, 40.59  $\text{mg}\cdot\text{g}^{-1}$  for effluent wastewater and 35.47  $\text{mg}\cdot\text{g}^{-1}$  for influent wastewater, respectively.

### 3.4 Breakthrough Curves

Column tests were performed to describe the sorption of the VP on selected sorbents under kinetic conditions using breakthrough curves. For each VP and each sorbent, these tests were carried out separately. WWTP effluent water was used as a matrix for all these tests. The initial concentration was derived from the  $q_m$  value of the Langmuir equation measured in the WWTP effluent water with the assumption of reaching 50% of the input concentration within 1 h. The resulting  $C/C_0$  vs.  $t$  breakthrough curves are shown in Fig. 4A, C, and E. The column adsorption capacity at 50% inlet concentration was calculated according to Eq. (4). The  $q_{50}$  value is expressed as the adsorbed amount of VP in mg or  $\mu\text{g}$  per gram of sorbent.

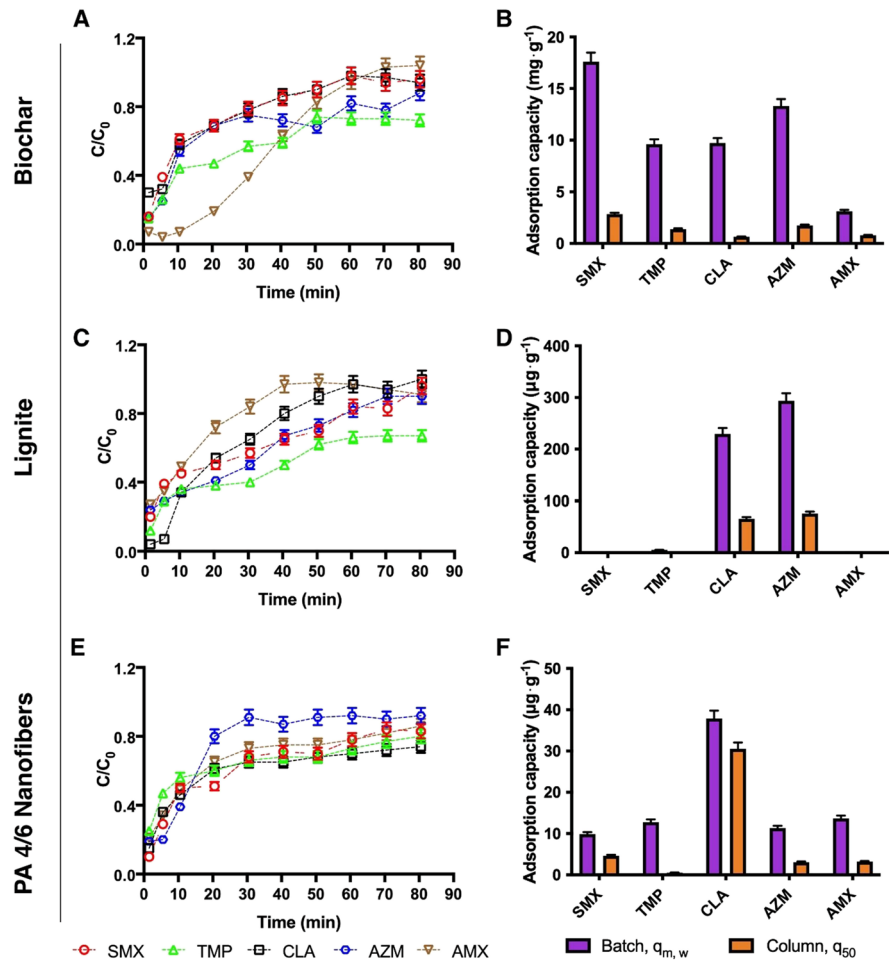
According to Fig. 4B, it can be seen that the sorption capacities decreased for biochar compared to

$q_{m,w}$  measured in WWTP effluent water. The highest decrease was observed for CLA (93.31%,  $q_{50} = 0.65 \text{ mg}\cdot\text{g}^{-1}$ ) > AZM (86.94%,  $q_{50} = 1.74 \text{ mg}\cdot\text{g}^{-1}$ ) > TMP (85.54%,  $q_{50} = 1.39 \text{ mg}\cdot\text{g}^{-1}$ ) > SMX (83.87%,  $q_{50} = 2.84 \text{ mg}\cdot\text{g}^{-1}$ ) > AMX (74.52%,  $q_{50} = 0.79 \text{ mg}\cdot\text{g}^{-1}$ ).

The influence of the experimental setup could be found in the study of Puga et al. (2022) with biochar in the relationship with venlafaxine, trazodone, and fluoxetine. A similar conclusion was reached by Caliskan Salihi and Tulay (2022) in their study concerning the relationship between carbon nanotubes and triflupromazine. A similarly large decline was recorded for lignite: TMP (98.12%,  $q_{50} = 0.10 \mu\text{g}\cdot\text{g}^{-1}$ ), AMX (96.12%,  $q_{50} = 0.04 \mu\text{g}\cdot\text{g}^{-1}$ ), SMX ( $q_{50} = 89.39\%$ , 0.19  $\mu\text{g}\cdot\text{g}^{-1}$ ), AZM (74.21%,  $q_{50} = 75.73 \mu\text{g}\cdot\text{g}^{-1}$ ), and CLA (71.42%,  $q_{50} = 65.56 \mu\text{g}\cdot\text{g}^{-1}$ ). Nanofibers showed the slightest decrease, except for TMP. In the case of TMP, sorption was reduced by 95.85% (0.53  $\mu\text{g}\cdot\text{g}^{-1}$ ), followed by AMX (76.52%,  $q_{50} = 3.21 \mu\text{g}\cdot\text{g}^{-1}$ ), AZM (72.94%,  $q_{50} = 3.06 \mu\text{g}\cdot\text{g}^{-1}$ ), SMX (53.04%,  $q_{50} = 4.63 \mu\text{g}\cdot\text{g}^{-1}$ ) and CLA (19.38%,  $q_{50} = 30.54 \mu\text{g}\cdot\text{g}^{-1}$ ). The adsorption kinetics of nanofibers might also be explained by the fact that PA 4/6 has a high tendency to swell by water uptake (Adriaensens et al., 2001; Francisco et al., 2019; Monson et al., 2008). The swelling may lead to the reduction of pore (and mesopore) size and an increase in fiber volume, which in turn hinders further adsorption of VP. This hypothesis partially corresponds with the kinetics in Fig. 3A, C, E, where nanofibers approach saturation values faster than the other two sorbents. To the best of our knowledge, there are no in-depth studies regarding the comparison of sorption capacities of selected pharmaceuticals, neither by PA 4/6 nanofibers nor lignite obtained via similar experimental setups.

Biochar again showed the highest sorption capacities even though the values were significantly influenced by WWTP effluent water use and test type. Lignite is suitable for the sorption of lipophilic compounds, as mentioned above. For these two materials, the influence of the homogeneity of the filling is evident. Higher inhomogeneity may result in creation of a preferential pathway for the liquid without contacting (wetting) the sorbent as a whole. It is, therefore, beneficial to treat biochar and lignite appropriately to avoid incomplete contact if possible. In the case of nanofibers, it is easier to fill the column homogeneously due to the presence of a carrier. The significant

**Fig. 4** Results of column test in WWTP effluent water. The left panel (A, C, and E) represents the breakthrough curves and the right panel (B, D, and F) comparison of  $q_m$  and  $q_{50}$  for a given VP and sorbent in WWTP effluent water



difference in the case of  $q_m$  may be due to insufficient contact between the liquid phase and the sorbent, and insufficient dwell time also caused by setting a higher flow rate. The estimated dwell time here was lower than the time required reaching sorption equilibrium. In this respect, it would be advisable to consider sufficient quantities of sorbent and experimental parameters to ensure satisfactory results. Indeed, this study has several limitations. First of all, the attempt to conduct experiments with similar reaction conditions to those found at contaminated sites. In these cases, for example, pH adjustment is not readily feasible, which may be critical for the sorption of some compounds (Huang et al. 2020). At the same time, low-cost and commercially available materials were used. These materials could be used in the implementations without any prior adjustment.

Further research should focus on other suitable substrates or their combination. Nevertheless, it is advisable to verify the suitability of the sorbent for the chemicals in question under the conditions expected at the contaminated site, such as the arrangement of the sorption apparatus or the type of WWTP effluent water regarding the high composition variability. For real applications, it would be helpful to attend to optimizing parameters for column tests such as flow rates or fixed-bed length. Furthermore, lifetime and recyclability are two other elements that influence the use of sorbents in practice. Therefore, long-term experiments and experiments involving substrate purification and reuse processes should be carried out. An interesting element of further research may be the microbial analysis of bacteria responsible for drug degradation or monitoring changes in the bacterial consortium during longer-term experiments.

## 4 Conclusion

The performed study demonstrated the sorbents' sorption properties for selected VP in different matrixes and experimental setups. Using ultrapure and WWTP effluent water as batch test medium showed a decrease in sorption capacities by 6.31 to 72.15% for biochar, 25.58 to 98.55% for lignite, and 4.21 to 67.71% for PA 4/6 nanofibers. Consequently, beyond the properties of sorbents, such as specific surface area and presence of functional groups, and physicochemical properties of VP, the effect of WWTP effluent water ballasts has been demonstrated. Another sorption capacity decrease was the consequence of experimental setup changes. The  $q_{50}$  values obtained from the dynamic column test with WWTP effluent water were 0.65–2.84 mg·g<sup>-1</sup> for biochar, 0.04–75.73 µg·g<sup>-1</sup> for lignite, and 0.53–30.54 µg·g<sup>-1</sup> for nanofibers. These results suggest that biochar can be used as a non-selective sorbent in high pollution levels. In contrast, lignite and nanofibers are more suitable for less contaminated sites or as an auxiliary component of water treatment apparatus sorbents in the implementation of running water field conditions.

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**Data Availability** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Declarations

**Competing Interest** The authors declare no competing interests.

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