

Article

Treatment of Wastewater from Soil Washing with Soluble Humic Substances Using Biochars and Activated Carbon

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Abstract: Energy can be obtained by pyrolysis of organic wastes, and the solid residue of pyrolysis (biochar) can be used as an adsorbent for the treatment of various types of wastewater. Although soil washing can effectively remediate metal-contaminated soils, it can generate significant amounts of soil washing wastewater (SWW). This study investigated the effectiveness of using activated carbon and various biochars to treat SWW from the remediation of soil heavily contaminated with cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) with soluble humic substances (SHS) from municipal sewage sludge. Willow biochar (BW), plant biomass biochar (BPB), coconut shell biochar (BCH), and Norit SX2 activated carbon (ACN) were tested at different dosages (12.5–100 g/L) and adsorption times (30–1440 min) for the treatment of SWW. At 100 g/L dosage, biochar removed Cd, Cu, Ni, Pb, and Zn with 56–83%, 32–41%, 18–42%, 75–83%, and 44–83% efficiency, respectively, while ACN removed them with 87–95% efficiency. Only BW and ACN removed soluble organics with efficiencies of 49% and 94%, respectively, at the highest dosage. Adsorption of metals and soluble organics was mainly controlled by physisorption and chemisorption. Diffusion of metals and soluble organics into the different pore sizes was not the most important rate-limiting step. ACN and BW had better structural properties and treated SWW most effectively. BPB and BCH removed metals but not soluble organics, which could be beneficial for SHS recycling.

Keywords: soil washing; treatment; adsorption; pyrolysis; biochar; heavy metals; humic substances; soluble organics



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1. Introduction

Soil washing is one of the most widely used and studied off-site techniques for remediating metal-contaminated soil [1]. Some conventional washing agents used in soil washing (e.g., acids, EDTA) can diminish the quality of the treated soil. Nowadays, there is a trend toward using new-generation washing agents in the form of naturally soluble organic substances to minimize harmful effects on the physicochemical properties of the washed soil and to make remediation more sustainable [2,3]. The main sources of these novel agents can be geochemical resources, unprocessed wastes (e.g., municipal sewage sludge, agricultural wastes), and processed wastes (e.g., residue after anaerobic digestion, compost) [4]. Utilizing waste as a source of washing agents for soil washing is consistent with the principles of a circular economy. In the previous studies, it was demonstrated that soluble humic substances (SHS) derived from municipal sewage sludge could serve as an alternative washing agent to synthetic EDTA. SHS from sewage sludge contains fulvic

acids (FAs) and humic acids (HAs), and they possess great potential for remediating soils highly polluted with Cu, Pb, and Zn (removal efficiency of 60–90%), promote recovery of soil function, and have limited soil toxicity [5,6].

Treating soil with a given washing agent generates large amounts of soil washing wastewater (SWW) [7,8], also known as spent soil washing solution [1]. Real SWW have complex compositions. They contain soluble metals at different concentrations, residual spent washing solution, competing cations washed from the soil, and other coexisting soil contaminants [7,9–11]. The resulting physicochemical properties of SWW (e.g., pH, conductivity, contaminant concentrations) can vary substantially depending on the type of soil remediated, the type and concentration of contaminants, the type and properties of the washing solution, and the operating conditions used for soil washing.

For example, the SWW from soil treatment with FeCl_3 contained high concentrations of Zn (212.5 mg/L) and Cd (84.4 mg/L) [12]. For comparison, SWW from soil treatment with EDTA had an initial pH of 6.64 and contained metals at various concentrations: 258 mg/L of Pb, 290.1 mg/L of Zn, 5.9 mg/L of Cu, and 1.8 mg/L of Cd [8]. The SWW produced by soil washing with NaOH mixed with an amphoteric surfactant had an alkaline pH (13.1) and high concentrations of inorganic and organic pollutants: 14.5 mg As/L, 2.41 mg Cr/L, 8.22 mg Cu/L, 6.42 mg/L of pentachlorophenol, and 127 ng/L of polychlorinated dioxins and furans [13]. Due to its complex composition, a complete treatment of SWW can be challenging. Nevertheless, SWW should be treated before final disposal, or it can be regenerated and reused for subsequent soil treatments. Proper disposal of SWW is an essential part of a complete remediation process.

So far, experiments on the treatment of SWW have been conducted mainly with conventional washing agents such as chelating agents, i.e., EDTA, EDDS [8,14], HCl solutions [7,10], FeCl_3 solutions [12,15]; and plant biosurfactants, e.g., saponin, with the aim of recovering these agents and making the soil remediation process more cost-effective [16]. Adsorption, precipitation, advanced oxidation processes, and membrane technology can be used to treat SWW [16]. A combination of soil washing with selective adsorption of pollutants from SWW and final disposal of the adsorbent [17] may be an important alternative due to its high efficiency, lower cost, and ease of operation compared to other methods [18]. Recently, adsorbents tested for treating SWW from the washing of metal-contaminated soils have mainly included agricultural wastes, e.g., garlic peels [19] and coffee grounds [7], metal oxides in modified nanoparticles [20], or graphene oxide [10].

The growing demand for sustainable and renewable energy sources has led to increased interest in converting biomass into valuable bioproducts through pyrolysis. Biochar, as a solid carbon bioproduct, is a well-known adsorbent for removing complex inorganic and organic contaminants. Current research aims to replace activated carbon with biochar to reduce the cost of treatment processes and take advantage of the specific properties of biochar. The properties of biochar depend on the type of feedstock, the technology used to pre-treat the feedstock, the thermal process, and the post-treatment of the biochar. Due to its porous properties, high surface area, and functional groups, such as phenol, hydroxyl, and carboxyl groups, biochar is highly adsorbent [21]. Biochar is an attractive adsorbent also due to its low cost of production, economic advantages, possibility of conversion to biochar, and wide availability of raw materials [22,23].

The biomass for producing biochar comes from a wide range of organic materials, such as plant residues, sewage sludge, manure, agro-industrial biomass, etc. Thus, biochar production enables improvements in waste management and sustainable resource utilization. Biochar is becoming increasingly important as a solution for the removal of pollutants in industry and agriculture to improve environmental quality. It has great potential for treating various types of wastewater, such as industrial, municipal, and agricultural waters, as well as stormwater [24]. Its ability to simultaneously remove inorganic and organic pollutants makes it a potentially suitable adsorbent for treating SWW generated by washing soils contaminated with heavy metals. Biochar is a popular additive for immobilizing metals in contaminated soils, but its application for treating SWW is a new approach. There is

only one paper in the literature on applying pristine and modified biochar for treatment of FeCl_3 SWW after washing soil contaminated with Cd, Cu, Pb, and Zn [12]. In general, there is a lack of information on the treatment of wastewater generated by soil washing with “green” washing agents [1], such as soluble humic substances (SHS) recovered from waste. Given the advantages of adsorption processes for treating wastewater and post-treatment waters and the possibility of using biochar to remove complex pollutants, the present study aimed to compare the efficiency of biochar produced from different feedstocks with that of commercial activated carbon (as a reference adsorbent) for treating SWW from soil remediation with SHS from municipal sewage sludge at various adsorbent dosages, and adsorption times. We hypothesized that willow biochar, mixed plant biomass biochar, and coconut shell biochar would have different effects when used to treat SWW from soil washing with SHS.

2. Materials and Methods

2.1. Soil Characterization and SHS Preparation

For remediation, soil spiked with high levels of Cd, Cu, Ni, and Pb and aged for two years (at room temperature and a moisture content of 65% of its water holding capacity) was used. The soil had the following characteristics: loamy texture, pH in KCl of 6.3, organic matter of 10.6%, 47 mg/kg (Cd), 1020 mg/kg (Cu), 498 mg/kg (Ni), 4094 mg/kg (Pb), and 2110 mg/kg (Zn).

Soluble humic substances (SHS) extracted from dried and ground municipal sewage sludge from the municipal wastewater treatment plant in Olsztyn (Poland) were used as washing agents for soil treatment. Previous research has shown that municipal sewage sludge is an important source of SHS [6]. The full procedure for SHS extraction has been described in [25]. Briefly, prior to SHS extraction, the sewage sludge was pretreated with distilled water to remove non-humus substances (e.g., sugars and proteins) and defatted with a mixture of chloroform:methanol to remove fats, waxes, and bitumen in a MarsXpress microwave oven (CEM, Corporation, Matthews, NC, USA) at 65 °C [16]. The extraction of SHS was conducted with 0.1 M NaOH for 24 h. Then, the suspension was centrifuged and filtered with a 0.45- μm filter. The concentration of the obtained SHS was 3654 mg TOC/L. For soil washing, the SHS was diluted with water, and the pH was adjusted with 1 M HNO_3 .

2.2. Soil Washing with SHS

Batch soil washing was performed at a ratio of soil to SHS of 1:40 (*w/v*) in polyethylene tubes for 24 h. Samples were shaken using an Intelli-Mixer RM-2L. After washing, the supernatants were separated from the soil by centrifugation and filtration through a 0.45 μm filter. The solution from soil washing is referred to as soil washing wastewater (SWW). The characteristics of the SHS and SWW are compared in Table 1.

Table 1. Characteristics of SHS and SWW solutions (mean $\pm$ SD, $n = 3$).

Property	Unit	SHS	SWW
pH	-	4.0 $\pm$ 0.1	4.9 $\pm$ 0.1
Electrical conductivity	mS/cm	36.6 $\pm$ 4.5	64.9 $\pm$ 1.5
Total organic carbon		2200.0 $\pm$ 20.6	1934.0 $\pm$ 11.6
Total inorganic carbon		6.5 $\pm$ 0.6	6.4 $\pm$ 0.2
Calcium (Ca)		15.6 $\pm$ 2.6	127.6 $\pm$ 6.5
Magnesium (Mg)		15.1 $\pm$ 1.9	29.9 $\pm$ 3.2
Sodium (Na)		1025.5 $\pm$ 8.9	1022.9 $\pm$ 10.6
Cadmium (Cd)	mg/L	0.1 $\pm$ 0.02	0.5 $\pm$ 0.08
Copper (Cu)		6.1 $\pm$ 0.4	10.3 $\pm$ 1.3
Nickel (Ni)		0.1 $\pm$ 0.03	3.1 $\pm$ 0.6
Lead (Pb)		0.05 $\pm$ 0.1	7.8 $\pm$ 0.02
Zinc (Zn)		3.0 $\pm$ 0.3	14.2 $\pm$ 0.9

2.3. Types of Adsorbents and Their Characterization

Three types of biochar were made from pyrolysis at 650 °C (pyrolysis time 15 min, heating rate 3 °C/s) of willow biomass (BW); a mixture of plant biomass, including willow, alder, and oak (BPB); and coconut husks (BCH) (Fluid S.A., Sędziszów, Poland) and then used to treat SWW via batch adsorption. As a reference adsorbent, commercially available Norit SX2 activated carbon (ACN) was purchased from Chempur Company (Piekary Śląskie, Poland) (Figure 1).



Figure 1. Adsorbents used for treatment of SWW: (a) BW, (b) BPB, (c) BCH, and (d) ACN.

For the experiment, the biochars were crushed and sieved through a 1 mm sieve. The ACN was used in the original form provided by the manufacturer. The adsorbents were characterized in terms of their textural properties (surface area, pore volume, and pore size); content of moisture, volatile matter, ash, fixed carbon, and elemental composition; pH; electrical conductivity (EC); total heavy metals (Cd, Cu, Fe, Ni, Pb, and Zn); and macroelement concentrations (Ca, Mg, and Na). In addition, a qualitative analysis of surface oxygen-containing functional groups and a mineralogical analysis were performed.

2.4. Treatment of SWW

The SWW was treated with the biochars and ACN under batch laboratory conditions. The effectiveness of SWW treatment with the tested sorbents was determined depending on:

- The adsorbent dosage (12.5; 25; 50; and 100 g/L): in this experiment, 20 mL of SWW was shaken at different adsorbent dosages for 24 h at 90 rpm; then samples were centrifuged at 8000 rpm for 10 min and filtered through a 0.45 µm filter;
- Adsorption time (30, 60, 120, 180, and 1440 min): this experiment was performed with an adsorbent dosage of 100 g/L; the samples were prepared in the same way as in the previous experiments.

In the treated SWW, the following characteristics were determined: pH, conductivity, and concentrations of total organic carbon (TOC), heavy metals (Cd, Cu, Ni, Pb, and Zn), and macroelements (Ca, Mg, and Na).

2.5. Analytical Methods

A pH meter (HI 221, Hanna Instruments, Woonsocket, RI, USA) and a conductivity meter (HI 8733, Hanna Instruments, Woonsocket, RI, USA) were used to measure both pH and electrical conductivity (EC) of distilled water extracts (1:10 *w/v*). To determine moisture content, volatile matter (VM) content, ash content, and fixed carbon, proximate analyses were performed on the sample by drying it at 105 °C for 18 h, 950 °C for 10 min, and 750 °C for 6 h. Using 1–3 mg of the finely ground and sieved sample, the elemental composition of the adsorbents (C, H, and N) was analyzed using a FLASH 2000 elemental analyzer (Thermo Scientific, MA, USA). The oxygen content was calculated from the difference, including C, H, N, and ash. The H/C and O/C molar ratios of the adsorbents were calculated on the basis of their elemental compositions. The pore size distribution was calculated using the Barret–Joyner–Halenda method (Micrometrics ASAP

2420 M, Norcross, GA, USA) based on the desorption plot of the N₂ adsorption-desorption isotherm. The Brunauer-Emmet-Teller (BET) specific surface area was calculated by fitting the BET equation to the linear part of the BET plot. Fourier transform infrared spectra with attenuated total reflectance (FT-IR/ATR) were recorded in the 3600–600 cm^{−1} range with 4 cm^{−1} resolution at room temperature (Nicolet 6700 spectrometer and Meridian Diamond ATR accessory; Harrick, NY, USA). Samples were applied directly to the diamond crystal prism and brought into intimate contact with the diamond surface by a pressure tower. The interferograms of each spectrum from 512 scans were averaged. ATR spectra were recorded using dry potassium bromide (48 h, 105 °C) as reference material. All ATR spectra were corrected for carbon dioxide and water vapor. No smoothing algorithms were applied. At least three replicates were performed for each spectral measurement. Mineralogical XRD analysis of the adsorbents was performed using an X'Pert Pro diffractometer with an X'Celerator Scientific detector (Malvern Panalytical, Malvern, UK) at an angular range of 7–120° (2Theta). X-ray photoelectron spectroscopy (XPS) was performed using the multi-chamber UHV system (PREVAC, Rogów, Poland). The hemispherical Scienta R4000 electron analyzer was used to obtain the spectra. A complementary piece of equipment was the Scienta SAX-100 X-ray source (Al K, 1486.6 eV, 0.8 eV band) coupled with the XM 650 X-ray Monochromator (0.2 eV band). The pass energy of the analyzer was set to 50 eV for regions (high resolution spectra): C1s, O1s, and N1s with a 50 meV step and 200 eV for survey spectra (with a 750 meV step). The analytical chamber had a base pressure of 2×10^{-9} mbar. It did not rise above 3×10^{-8} mbar during the spectrum collection. All the spectra processing and fitting were performed using CasaXPS software v. 2.3.25. For quantitative analyses, theoretical cross-sections were used. Envelopes of C1s and O1s spectra were fitted using asymmetric peaks for aromatic carbon components (line shape: LF(1.32,1.92,20,30,1)) and Gaussian–Lorentzian profiles (70% Gaussian, 30% Lorentzian) after applying Shirley backgrounds.

The concentration of SHS (as TOC) in the samples before and after the adsorption experiments was measured using a Shimadzu Liquid TOC-VCSN analyzer. To measure the total metal (Cd, Cu, Fe, Ni, Pb, and Zn) and macroelement concentrations (Ca, Mg, and Na), the dried adsorbent samples were digested in a MarsXpress microwave oven (CEM, Corporation, Matthews, NC, USA) with 6 mL of HNO₃ acid, 2 mL of H₂O₂, and 0.4 mL of HF acid. The samples were heated to 190 °C in 15 min, then digested at 190 °C for 20 min [26]. After cooling, the samples were filtered through Whatman 42 filters into volumetric flasks. The concentrations of heavy metals in the SHS, the SWW both before and after adsorption, and the digested adsorbents and soil were measured using a flame atomic absorption spectrometer (FAAS) (Varian, AA280FS, Mulgrave, Australia). Metals in soils were fractionated into exchangeable and acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions [27]. The accuracy of metal analysis by FAAS was validated by the analysis of CRM 142 R reference material.

2.6. Calculation and Statistical Methods

The adsorption capacities (q) and removal efficiencies (E) for heavy metals and soluble organics at different adsorption conditions were calculated using Equations (1) and (2):

$$q = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the concentrations of heavy metals or soluble organics (as TOC) in SWW before and after adsorption, respectively; m (g) is the mass of the adsorbent; and V (L) is the volume of SWW.

Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were employed to describe the adsorption kinetics of metals and soluble organics as given in Equations (3)–(5), respectively:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad (4)$$

$$q_t = k_i t^{0.5} + C_i \quad (5)$$

where q_e (mg/g) is the capacity of the adsorbent at a given time and equilibrium; k_1 (1/min) and k_2 (g/(mg·min)) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively; k_i (mg/g·min^{0.5}) is the rate constant of the intraparticle diffusion model; and C_i (mg/g) is the adsorption constant of the intraparticle diffusion model, which describes the effect of boundary layer thickness on adsorption.

The validity of the kinetic models was evaluated by the correlation coefficient (R^2) (Statistica 13.3). Adsorption experiments were performed in triplicate, and the mean and standard deviation are reported. A one-way analysis of variance (ANOVA) was performed to examine differences between treatments of SWW with BW, BPB, BCH, and ACN. Tukey's HSD test was performed to further analyze the significant differences identified by ANOVA (Statistica 13.3).

3. Results and Discussion

3.1. Metal Removal from Soil

Figure A1 (Appendix A) shows the distribution of heavy metals in the contaminated soil and the removal of heavy metals from the soil with the SHS in the single-stage soil washing process. In the spiked soil, aged for two years, the heavy metals occurred in varying total concentrations, which is typical for real contaminated soils. The removal of individual metals from heavy contaminated soils with SHS was differentiated, which was related to their total content, their distribution in the soil, and the affinity of SHS for individual metals. The heavy metal removal efficiency decreased in this order: Cd (44.3%) > Cu (40.4%) > Zn (27.0%) > Ni (25.2%) > Pb (7.6%). The highest removal was obtained for Cd, whose total concentration was the lowest and mobility (the proportion in the F1 fraction) the highest. Cd, such as Zn, is characterized by high mobility in contaminated soils, which increases under acidic conditions [25].

Although Zn was also mobile in soil, its removal efficiency was lower than that of Cd since the total concentration of Zn was about 45 times higher than that of Cd. Although Ni was more mobile than Cu (152.7 mg/kg of Ni and 126.3 mg/kg of Cu in the F1 fraction), the removal efficiency was higher for Cu than for Ni. Many studies confirm that SHS from various sources is effective in removing Cu due to the affinity of the carboxyl and phenolic groups of SHS to Cu [5,28,29]. In addition, the efficiency of metal removal through soil washing with SHS strongly depends on soil washing conditions [28]. The SHS can also be effective for Pb removal [29]. Under the soil washing conditions used in the present study (SHS concentration of 2 g/L, washing time of 24 h, single-stage washing), the removal efficiency of Pb was below 10%. The previous study, with the use of SHS extracted from compost, revealed that the efficiency of metal removal with SHS at a concentration of 2.1 g/L and pH 4 was comparable to those values obtained for SHS from sewage sludge: 44.1% (0.52 mg/L) for Cd, 22.1% (5.64 mg/L) for Cu, 17% (2.12 mg/L) for Ni, 12.9% (13.2 mg/L) for Pb, and 11% (5.80 mg/L) for Zn [25]. A considerable improvement in metal removal was observed after triple soil washing with SHS. Because the aim of this study was not the optimization of soil washing with SHS but the treatment of wastewater generated by soil washing, wastewater generated in single-stage soil washing was used.

3.2. Adsorbent Characterization

The selected physicochemical properties of the tested adsorbents are listed in Table 2. The adsorbents differed in their structural properties, including surface area, pore volume, and pore size. Total pore volume and surface area were highest for ACN and BW, providing more active sites for pollutant adsorption. Based on the micropore volume and total pore volume, the proportion of micropores in the total pore volume decreased in this order: BW (76%) < ACN (24%) < BPB (9%) < BCH (4%). The average pore diameter of BW and ACN was characteristic of mesoporous materials (2–50 nm) [30], while the average pore diameter of BPB and BCH was typical for macroporous materials (>50 nm). Surface area and porosity are the most important physical properties affecting the metal sorption capacity of biochar [21]. Additionally, pore size is important for the sorption of metals. Adsorption of large sorbates, regardless of their charge or polarity, onto biochar with small pore sizes may be limited [31], because mesopores are needed for their adsorption [32]. The structural properties of biochar vary significantly depending on the type of feedstock and the temperature of pyrolysis. Lignin-rich biomass (e.g., bamboo and coconut shells) produces microporous-structured biochar, while cellulose-rich biomass (e.g., shells) yields predominantly macroporous-structured biochar [33]. Jindo et al. [34] showed that, with an increase in pyrolysis temperature from 400 to 800 °C, the surface area of oak tree biomass increased from 5.6 to 398.1 m²/g, while that of risk husk biomass increased from 193.7 to 295.6 m²/g. In general, the surface area of biochar can vary over a wide range, from less than 1.0 to about 500 m²/g [35]. Some commercial activated carbons have a high surface area of nearly 1000 m²/g, a total pore volume of 0.5 cm³/g, and an average pore diameter of 2–3 nm [30,32].

Table 2. Physicochemical properties of adsorbents ($n = 3$, mean $\pm$ standard deviation).

Characteristic	Adsorbent			
	BW	BPB	BCH	ACN
Average pore diameter (nm)	5.3	127.0	128.6	7.2
BET surface area (m ² /g)	313.7	2.36	2.88	659.4
Micropore surface area (m ² /g)	272.9	0.52	0.29	347.3
Total pore volume (cm ³ /g)	0.1132	0.0089	0.0012	0.6116
Micropore volume (cm ³ /g) (%) *	0.0859	0.00077	0.00052	0.1456
	76	9	4	24
Moisture (%)	5.2	4.1	4.6	4.7
Volatile matter (%)	26.3	27.2	35.1	13.7
Ash content (%)	8.8	7.0	7.8	8.2
Fixed carbon (%)	59.7	61.7	52.5	73.4
pH	10.35 $\pm$ 0.29	7.90 $\pm$ 0.1	7.65 $\pm$ 0.09	9.58 $\pm$ 0.18
EC (mS/cm)	2.9 $\pm$ 0.0	2.0 $\pm$ 0.0	0.06 $\pm$ 0.0	1.2 $\pm$ 0.0
Total C (%)	75.27 $\pm$ 0.45	77.21 $\pm$ 2.32	67.64 $\pm$ 3.42	78.33 $\pm$ 0.64
Total H (%)	1.94 $\pm$ 0.13	2.14 $\pm$ 0.18	3.00 $\pm$ 0.05	0.71 $\pm$ 0.15
Total N (%)	1.78 $\pm$ 0.24	0.50 $\pm$ 0.09	0.90 $\pm$ 0.14	1.63 $\pm$ 0.09
Total O (%)	12.2	13.1	20.7	11.1
H/C mole ratio	0.31	0.30	0.53	0.11
O/C mole ratio	0.12	0.13	0.23	0.11

* The % value is the ratio of the micropore volume to the total pore volume $\times$ 100.

The content of volatiles in the tested adsorbents ranged from 13.7% (ACN) to 35.1% (BCH). Such values are typical for biochar produced at high pyrolysis temperatures, as the loss of volatiles is greater. All adsorbents contained a small amount of ash (7.0–8.8%), which is consistent with the data in the available references. Wood-derived biochar has an ash content of less than 10%, while non-wood-derived biochar has a high ash content (>50%) [36]. Ash contains potassium (K), calcium (Ca), magnesium (Mg), carbonates, and heavy metal compounds that prevent the formation of aromatic structures, which contribute significantly to the fixed carbon content [37,38]. In the present study, the fixed

carbon content in the adsorbents was high and ranged from 52.5% (BCH) to 73.4% (ACN), indicating that the adsorbents were highly stable.

All the adsorbents had an alkaline pH: BPB and BCH were slightly alkaline, while BW and ACN were more alkaline (pH of 10.35 and 9.58, respectively). The alkaline character of biochar is usually due to the presence of basic cations (mainly Ca, Mg, K, and Na), which are converted to oxides, hydroxides, and carbonates during pyrolysis, and to high electrical conductivity (EC), which indicates the presence of soluble salts. In the present study, BW and ACN had higher ash contents (8.8% and 8.2%, respectively) compared to the other biochars. BW had the highest EC, while ACN had the highest Na content (9.3 g/kg) (full data not shown). When biochar is produced at high temperatures, its content of basic cations (e.g., Na, Ca, and Mg) and carbonates increases while that of acidic functional groups decreases, contributing to a higher pH [21]. For example, when the temperature was increased from 200 to 800 °C, the basic functional groups on the surface of biochar prepared from *Conocarpus* waste increased from 0.15 to 3.55 mmol/g, while the acidic functional groups decreased from 4.17 to 0.22 mmol/g, which was reflected by the increase in the pH of the biochar from 7.37 to 12.4 [39]. Among the adsorbents tested in the present study, BW had the highest salinity (as EC), while BCH had the lowest salinity.

All the adsorbents had relatively high C contents (67.6–78.3%), which are typical of biochars produced at high temperatures and fulfilled the European Biochar Certificate (EBC) requirements for biochar quality (>50% d.m.). The contents of O, H, and N were progressively lower than those of C. The adsorbents had different H/C ratios, but all exhibited a high degree of carbonization and stability (H/C ratio < 0.7, according to [26]). As shown by the H/C ratio, ACN was the most condensed of the adsorbents, while BCH was the least condensed. These results were consistent with those regarding the volatile matter and fixed carbon contents (Table 2). During pyrolysis, the increase in C content due to polymerization, dehydration, and volatilization is inversely related to the change in H content. The H content is lost through dehydration, while the C content increases through condensation and graphitization, which affect the H/C ratio [38].

The adsorbents had relatively low molar ratios of O/C (0.11–0.23), which could be due to the fact that the biochars were prepared at high temperatures (650 °C), favoring a greater loss of H and O than of C [34]. The H/C and O/C ratios indicate that BW and ACN were more hydrophobic than BPB and BCH. These properties can be important for the treatment of SWW, which contains SHS, heavy metals, and some macroelements. Aromatic and aliphatic moieties in biochar have been found to be important for the sorption of organic compounds [40].

The XPS spectra of BW, BCH, BPB, and ACN are shown in Figure 2a, and their surface elemental compositions are listed in Table 3. The XPS confirmed that C and O were the main components of the adsorbents. BCH contained the least amount of surface C, 84.0%at. (atomic percentage), while the content in ACN exceeded 91.4%at. The amount of O was lowest in ACN (7.7%at.). In the other adsorbents, the content ranged from 11.5 to 14.5%at. Small amounts of N and Ca or Si were present in all adsorbents, which can be attributed to the composition of the raw biomass used as substrates. The individual spectra of the materials studied are shown in Figures A2–A5 (Appendix A). The elemental surface composition alone is not sufficient to explain the differences in the overall removal efficiency of the heavy metals. As mentioned earlier, aromatic/graphitic structures play an important role in the sorption of heavy metals due to the interactions of their π -electrons with the metals. To a lesser extent, carboxyl groups may also play a role. The results of fitting C1s spectra and O1s spectra are shown in Figures A6 and A7 and in Tables A1 and A2 (Appendix A). The concentration of surface aromatic structures was clearly highest in ACN, reaching 63.4%at. The percentage of such structures in BCH, BW, and BPB was 33.6, 29.1, and 40.3%at, respectively. These results are in agreement with the FTIR measurements (Figure 2c).

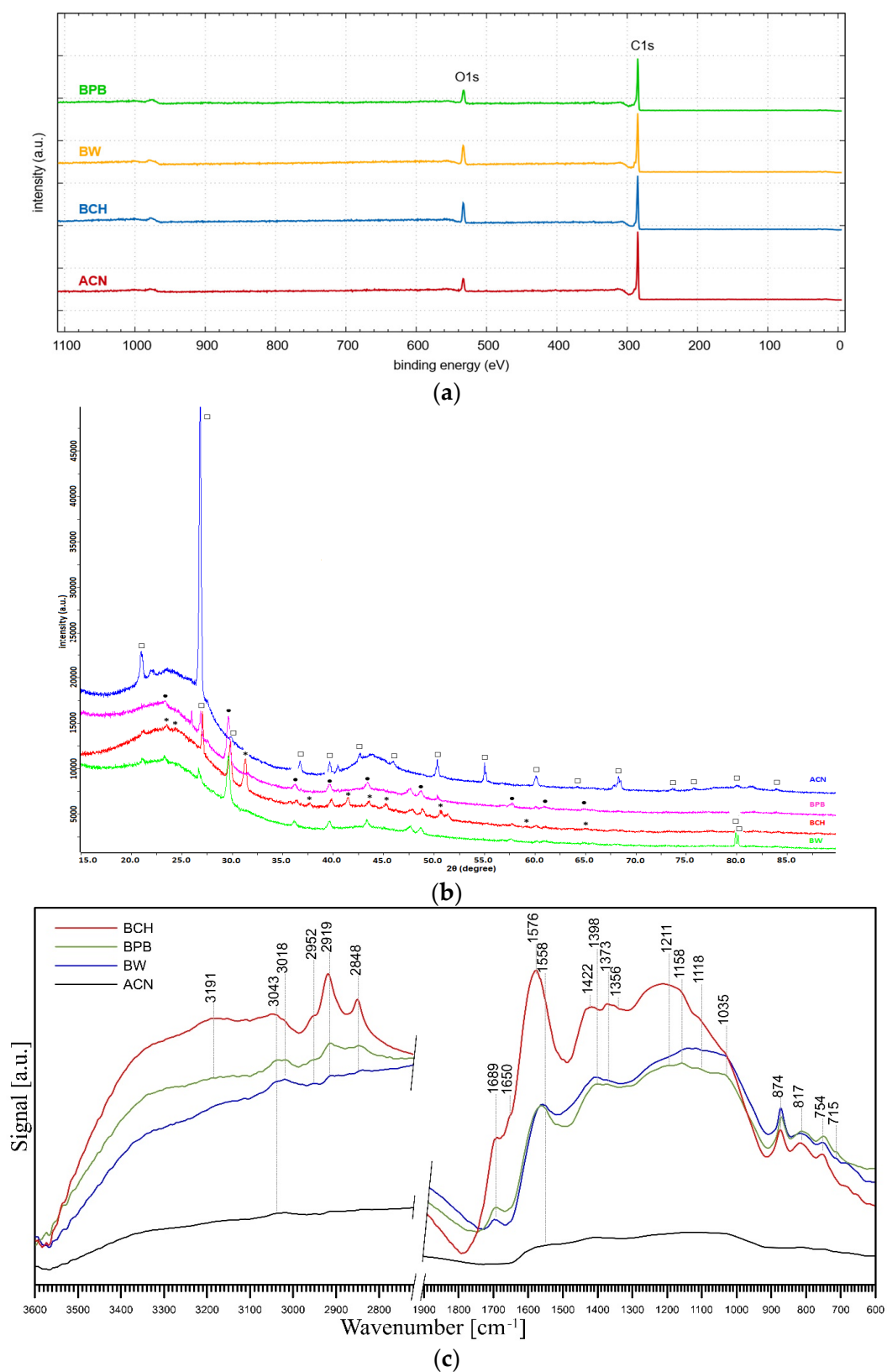


Figure 2. XPS spectra (a), XRD spectra (b), and FT-IR/ATR spectra (c) of studied adsorbents. The XRD spectra were matched with different colors: green for BW, pink for BPB, red for BCH, and blue for ACN (□ SiO₂ quartz; ● CaCO₃ calcite; * CaMg(CO₃)₂ dolomite).

Table 3. Surface elemental composition of adsorbents (atomic percents) determined by XPS.

Adsorbent	Element	Binding Energy (eV)	Conc. (%at.)
BW	C	285.0	85.2
	N	399.8	0.8
	O	533.3	13.5
	Si	103.5	0.4
BPB	C	285.0	87.2
	N	399.8	0.6
	O	532.5	11.5
	Ca	347.3	0.7
BCH	C	285.0	84.0
	N	399.0	1.2
	O	533.3	14.4
	Ca	348.0	0.5
ACN	C	285.0	91.4
	N	402.0	0.5
	O	533.3	7.7
	Si	102.8	0.4

Several principal bands can be observed in the FT-IR/ATR spectra of adsorbent samples (Figure 2a). The band at $\sim 3200\text{ cm}^{-1}$ is responsible for the presence of O–H groups in carboxylic acids [41,42].

The band at about 3043 cm^{-1} , which is the most intensive in the FT-IR/ATR spectrum of the BCH sample, is attributed to =C–H stretching in aromatic structures. The presence of these structures can be confirmed by analyzing the spectral range below 1600 cm^{-1} , where relatively intense bands at 1576 cm^{-1} (BCH spectrum) and 1558 cm^{-1} (BW and BPB spectra) as well as multiple bands within the $880\text{--}700\text{ cm}^{-1}$ range (aromatic structures out-of-plane bending modes) [42,43] are present. The lowest intensity of the bands indicating the presence of aromatic structures is visible in the spectrum of the ACN sample. However, the band at $\sim 1576\text{ cm}^{-1}$ may be attributed to both C=C stretching in aromatic structures and C=O stretching in ketones, quinones, and/or carboxylates [44]. Similarly, the band at $\sim 3043\text{ cm}^{-1}$ may be the result of the overlapping of both stretching modes of aromatic and/or unsaturated aliphatic hydrocarbons [45]. The bands of aliphatic C–H stretching, mainly $-\text{CH}_3$ substituents of aromatic rings (2952 and 2848 cm^{-1}) and methylene bonds connecting aromatic rings ($-\text{CH}_2-$ at 2919 cm^{-1}), are present in all biochar spectra. These bands are the most intensive in the BCH spectrum.

The presence of C=O groups is confirmed by the shoulders at 1689 and 1650 cm^{-1} (aldehyde/ketone, carboxyl) [42]. Peaks between 1422 and 1035 cm^{-1} indicate the presence of C–O and O–H in alcoholic, phenolic and carboxylic groups (1356 cm^{-1}) or C–O–C stretching in ethers. Bands indicating the C–H deformation in aromatic structures can also appear within this range ($1200\text{--}1000\text{ cm}^{-1}$). Additionally, the presence of bands of inorganic compounds in biochars (i.e., carbonates, sulfates, phosphates, and silica) cannot be excluded. The wide band in the range of $1300\text{--}1000\text{ cm}^{-1}$ may have the contribution of both oxygen functional groups (e.g., C–O) and stretching vibrations of Si–O–Si bridges in quartz. The vibrations of the carbonate ions may also have a contribution in ~ 1409 , ~ 1100 , and 874 cm^{-1} bands [41]. These data can be confirmed by XRD analysis (Figure 2b). The intensity of oxygen functional group bands is the highest for BCH biochar, and the O/C mole ratio value seems to confirm it (Table 2). Those bands have a lower but similar intensity for BW and BPB samples, and the O/C molar ratio for these biochars is also similar. Spectroscopic data are therefore consistent with the physicochemical characteristics of the examined biochars.

3.3. The Effect of Adsorbent Dosage on SWW Treatment

3.3.1. Changes in pH and EC

The application of the adsorbents at different dosages changed the pH and EC in the treated SWW (Figure 3). Initially, SWW was strongly acidic (pH 4.88). The addition of the lowest dosage of BW (12.5 g/L) considerably increased the pH to an alkaline value (7.49); the same dosage of ACN increased it to a nearly neutral value (6.97); and the same dosages of BPB and BCH increased the pH by lesser amounts (to pH 5.88–5.95). As the dosage of each of the adsorbents was increased, the pH of the treated SWW also increased, with the values being highest at a dosage of 100 g/L (Figure 3a). At this dosage, the pH in the SWW treated with BW, ACN, and BPB was alkaline (pH 8.26, 7.94, and 7.26, respectively), while the pH in the SWW treated with BCH remained somewhat acidic (6.26). BW biochar increased the pH to the greatest extent, indicating that it has the highest alkalinity of the four adsorbents. BCH increased the pH by the smallest amount, which may indicate that it has a lower ion-exchange capacity compared to other adsorbents.

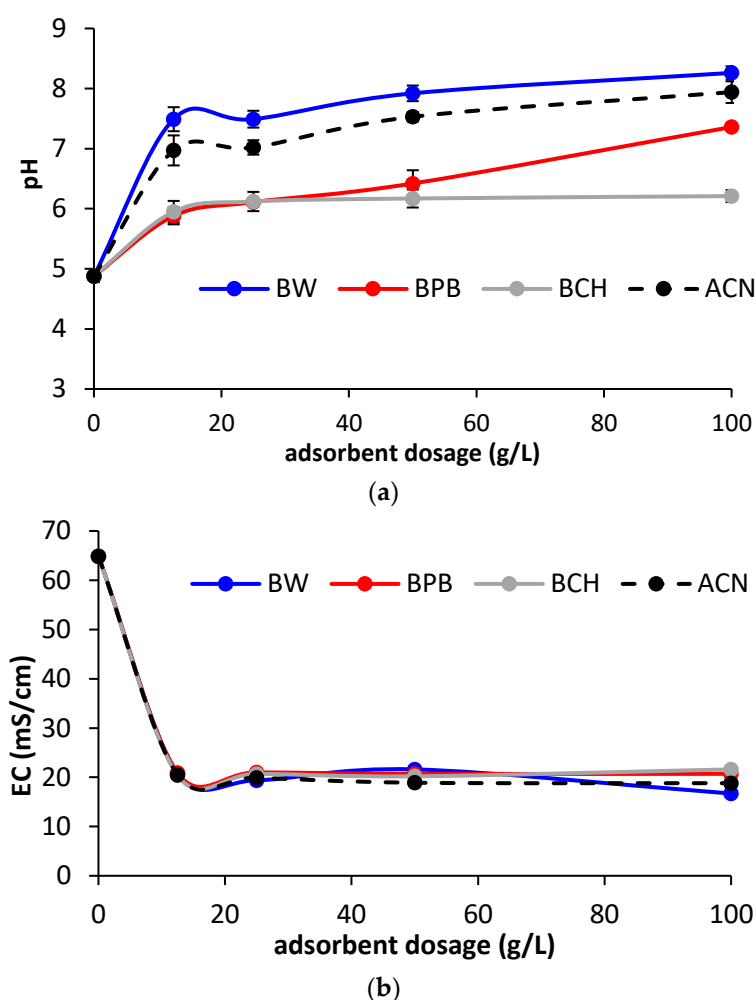


Figure 3. Values of pH (a) and EC (b) in SWW after addition of adsorbents at different dosages (sorption time 24 h, SWW concentration 1.9 g TOC/L) ($n = 3$, for EC standard deviation $\pm(0.1\text{--}0.5)$).

All of the adsorbents lowered the EC in the SWW. At the lowest dosage of the adsorbents, the EC in the SWW was more than 3-fold lower than it was before adsorption (Figure 3b). Although the use of BW biochar at the highest dosage (100 g/L) lowered the EC by the largest amount, from 65 to 11.7 mS/cm, increasing the dosages of the adsorbents beyond 12.5 g/L did not result in substantial further changes to the EC. The

decreases in the EC of the SWW can be connected to the sorption of different dissolved ions affecting salinity.

In the present study, the concentrations of three representative constituents of salinity (Na, Ca, and Mg) were monitored. The concentrations of the investigated alkali cations in the treated SWW are shown in Table 4. The removal of Na, Ca, and Mg from SWW with the different adsorbents varied depending on the type of adsorbent and its dosage. A concentration of these alkali cations that is lower than their initial concentration indicates that they were sorbed onto the adsorbents (positive values of RE), whereas a higher concentration indicates that they were released from the adsorbent during the adsorption process (negative values of RE). Such releases of alkali metals were particularly evident after treatment with BW biochar.

Table 4. Concentrations of Na, Ca, and Mg in SWW and their removal efficiency (RE) with different adsorbent dosages ($n = 3$).

Adsorbent	Dosage (g/L)	Na (mg/L)	RE (%)	Ca (mg/L)	RE (%)	Mg (mg/L)	RE (%)
BW	0	1022.9 ± 22.1		127.6 ± 5.9		29.9 ± 2.1	
	12.5	1167.9 ± 15.6	−14.2	182.6 ± 9.4	−43.1	57.9 ± 4.7	−93.9
	25	1167.7 ± 23.1	−14.2	179.8 ± 3.9	−41.0	58.6 ± 3.1	−96.3
	50	1041.8 ± 10.9	−18.0	129.0 ± 6.4	−1.2	49.6 ± 4.4	−66.2
	100	977.4 ± 8.9	4.4	88.0 ± 3.3	31.1	53.5 ± 4.9	−79.1
BPB	0	1022.9 ± 16.7		127.6 ± 2.7		29.9 ± 1.3	
	12.5	514.2 ± 9.1	49.7	145.3 ± 6.2	−13.9	40.1 ± 2.3	−34.3
	25	512.4 ± 5.9	49.9	162.0 ± 3.1	−27.0	25.7 ± 1.2	14.0
	50	495.4 ± 7.1	51.6	155.2 ± 2.9	−21.7	25.0 ± 0.9	16.2
	100	497.0 ± 7.3	51.4	158.1 ± 2.8	−23.9	42.7 ± 2.8	−43.0
BCH	0	1022.9 ± 19.1		127.6 ± 3.1		29.9 ± 1.0	
	12.5	520.3 ± 10.1	49.1	121.3 ± 1.2	4.9	51.5 ± 2.1	−72.3
	25	530.9 ± 8.2	48.1	121.9 ± 3.9	4.4	47.5 ± 3.7	−59.1
	50	501.5 ± 9.4	51.0	123.9 ± 4.1	2.9	47.6 ± 1.7	−59.5
	100	484.7 ± 7.2	52.6	146.6 ± 2.4	−14.9	74.9 ± 4.2	150.8
ACN	0	1022.9 ± 27.0		127.6 ± 4.1		29.9 ± 1.2	
	12.5	497.0 ± 18.1	51.4	98.9 ± 3.1	22.5	37.2 ± 0.9	−24.7
	25	489.3 ± 13.7	52.2	78.1 ± 3.8	38.7	32.7 ± 1.3	−9.5
	50	489.3 ± 10.6	52.2	61.1 ± 2.8	52.1	30.3 ± 1.0	−1.3
	100	488.8 ± 9.8	52.2	46.9 ± 1.9	63.3	21.4 ± 2.1	28.4

For example, Ca^{2+} and Mg^{2+} cations can be released from complexed functional groups (such as R–O–Me or R–COO–Me) as well as from Ca or Mg precipitates on the adsorbent surface. During the process, these complexes and precipitates may be dissociated or dissolved due to the acidic environment and/or the formation of new precipitates or complexes containing heavy metal cations [46]. Despite the poor removal of the analyzed alkali cations with BW biochar, the decrease in the EC in the treated SWW was similar to that observed with the other adsorbents. This suggests that other dissolved substances causing salinity (e.g., K, Fe, and SO_4) could be removed with the adsorbents, which was reflected by the decrease in the EC.

3.3.2. Removal of Heavy Metals

The efficiency of heavy metal removal at different dosages of adsorbents is shown in Figure 4. Although the heavy metal concentrations in the SWW were not high, the complex composition of the SWW meant that its treatment required higher dosages of adsorbents. The higher the dosage of the adsorbent, the greater the number of active sites available to bind metal ions, which leads to an increase in the efficiency of treatment. Removal of Cu, Ni, Cd, Pb, and Zn was highest with ACN at a dosage of 50 or 100 g/L. At these dosages, ACN treated SWW with the highest RE ($\geq 88\%$), which made it the most efficient among

those tested. Increasing the dosage tended to increase the adsorption efficiency of each biochar, and the highest efficiency of metal removal with the biochars was obtained at the highest dosage (100 g/L). BW biochar at dosages of 50 and 100 g/L can serve as an alternative to ACN for treating SWW contaminated with Cd (77–83% RE), Pb (77–83% RE), and Zn (78–83% RE). The BPB and BCH biochars removed Zn with lower efficiency (maximum RE 44–66%). With the use of the three biochars at a dosage of 100 g/L, the efficiency of Cu removal ranged from 32% (BCH) to 41% (BPB), while that of Ni removal ranged from 18% (BCH) to 42% (BW).

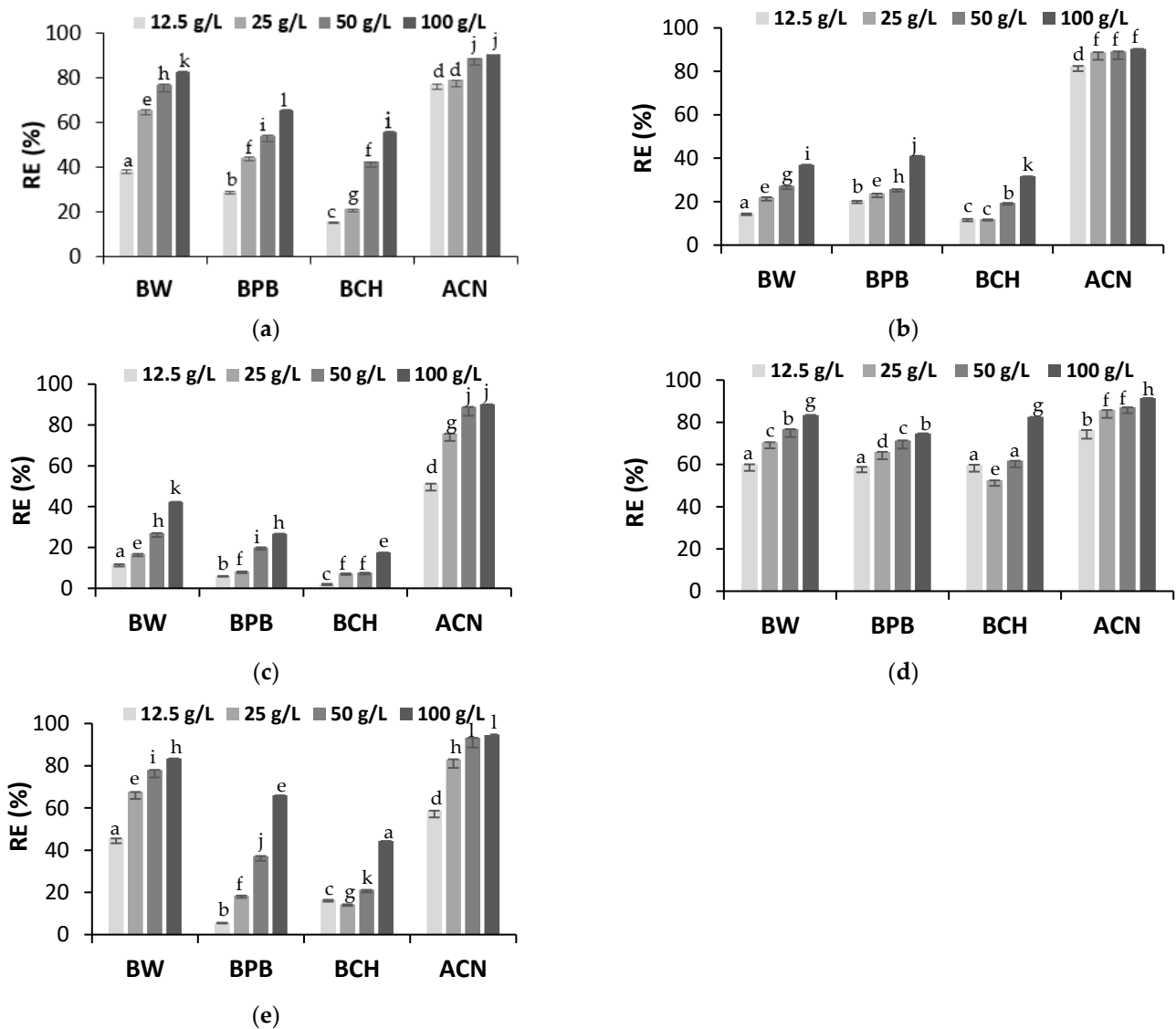


Figure 4. Removal efficiency (RE) of heavy metals from SWW at different adsorbent dosages: (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn (sorption time 24 h). For a given metal and specific dosage of adsorbent, values of RE followed by different letters are significantly different (ANOVA followed by Tukey's HSD test, $p < 0.05$).

When the dosage of biochar reaches a certain value, the adsorption capacity ceases to increase. Therefore, maximum removal can be achieved with the optimal dosage [47]. According to the obtained results, the optimal dosage for metal removal from SWW with ACN is 50 g/L. Such an optimal dosage cannot be given for the biochars because the metal removal efficiency increased almost linearly with the increase in biochar dosage.

Usually, the optimal biochar dosages for metal removal from aqueous solutions are much lower than the dosages that were used for metal removal from the SWW after soil washing. For example, Shan et al. [48] found that the optimum dosage of peanut shell biochar for Cd, Cu, Ni, Pb, and Zn removal from an aqueous solution was only 2 g/L. Chen et al. [49] found that, at a dosage of 10 g/L, $\geq 90\%$ of Cu and Zn were removed by corn straw biochar produced at 600 °C, and 40–70% of metals were removed with biochar made of a mix of hardwoods at 450 °C.

The major mechanisms controlling the sorption of metals by biochar from aqueous solutions include complexation, cation exchange between protons or alkali metals, precipitation, and electrostatic interactions [50]. The role that each of these mechanisms plays can vary greatly depending on the target metal [21]. The complexation of metals mainly involves interactions with functional groups. In addition, complexation can be facilitated via π -cation interactions with more aromatic and condensed adsorbent structures (linking metal d-electrons and C=C (π -electrons) through coordination bonds) [48,51]. The last mechanism may be particularly relevant for ACN, which had the lowest H/C ratio, the highest content of fixed carbon (Table 2), and the most aromatic structure according to XPS analysis.

Metal precipitation plays an important role in biochars containing carbonates, phosphates, sulfides, hydroxides, and silicates [52]. In the present study, the XRD patterns showed the presence of SiO₂ only (in ACN), CaCO₃ and SiO₂ (in BW, BPB, and BCH), and CaMg(CO₃)₂ (only in BCH) (Figure 2b), which could have been responsible for the formation of insoluble compounds with the metals. Fei et al. [52] demonstrated the participation of Si–O–Si bonds in the Cd sorption onto rice straw-derived biochar. According to Li et al. [53], silicates in biochar can provide sorption sites for Pb.

The role of electrostatic interactions between the negatively charged adsorbent and the positively charged metal could have differed depending on the type of adsorbent. All the adsorbents were prepared at high temperatures, which reduced the amounts of negatively charged functional groups (e.g., –COO–, –COH, and –OH). Based on the H/C and O/C molar ratios (Table 2) and FTIR spectra, the greatest role of functional groups in metal removal was for BCH, which had the highest abundance of hydroxyl and carboxylic groups, while ACN had the lowest abundance. Taking into consideration the higher pH of BW and ACN, these adsorbents could possibly have more deprotonated functional groups than BPB and BCH biochars.

Cation exchange could be a co-existing adsorption mechanism, especially with BW biochar (highest release of Na, Ca, and Mg, Table 4). Zhang et al. [54] showed that the amount of cations released from water hyacinth biochar (sum of K, Ca, Na, and Mg) was almost equal to the amount of Cd sorbed, suggesting that cation exchange plays a dominant role in Cd sorption by biochar and exchangeable cations may play a more important role in the sorption of metals than the surface area [52]. In the present study, the release of Na, Ca, and Mg was largest during SWW treatment with BW biochar, which may indicate that ion exchange plays a role in metal adsorption by this adsorbent (Table 4). Some alkali metals in biochar (such as Ca, Mg, K, and Na), which are retained by electrostatic effects, inner sphere complexes with carboxyl and hydroxyl groups, and precipitation, can be replaced by heavy metal cations in solution during the sorption process [46]. In situations where functional groups are not fully deprotonated, metals can also be adsorbed by exchange with protons from carboxyl and hydroxyl groups [55]. Such a mechanism is also possible in the present study. Lu et al. [46] showed that sludge-derived biochar at pH 5.0 adsorbed most of the Pb that was present by releasing Ca²⁺ and Mg²⁺ and by Pb complexation with COOH groups.

In this study, all the biochars effectively removed Pb. This could be because it is more easily hydrolyzed and has a larger ionic radius than the other metals. In addition, Pb has a greater affinity for surfaces than many other metals, which provides a competitive advantage in a coexisting system [51]. Taking into account the release of Ca, Mg, and Na from the biochars and the efficiency of Pb removal, cation exchange could be the

dominant mechanism of Pb removal by these adsorbents. With ACN, Pb complexation and precipitation might play more important roles [21] due to the reduced exchange of alkali cations (Table 4).

Considering the total pore volume, the average pore diameter of the adsorbents, and the ionic radii of the metal cations (0.097 nm for Cd, 0.073 nm for Cu, 0.069 nm for Ni, 0.119 nm for Pb, and 0.074 nm for Zn), adsorption through filling of the adsorbent micropores by metal cations may also have improved metal removal, especially in the cases of BC biochar and ACN [12].

The removal efficiency of Cu and Ni with BW, BPB, and BCH biochars was much lower than with can, which might be due to the greater competition of these metals with other coexisting components of the SWW for adsorption sites. Biochar has good removal efficiencies in single-metal systems but lower capacities in multiple-metal systems due to the competition between the heavy metals present in wastewater [55].

3.3.3. Removal of Soluble Organics

In this study, the concentration of soluble humic substances in the SWW after soil washing was assumed to be equal to the concentration of total organic carbon (TOC). To determine the changes in the concentration of organic compounds after treating the SWW with the adsorbents, TOC was also used. The changes in TOC in the treated SWW are shown in Figure 5.

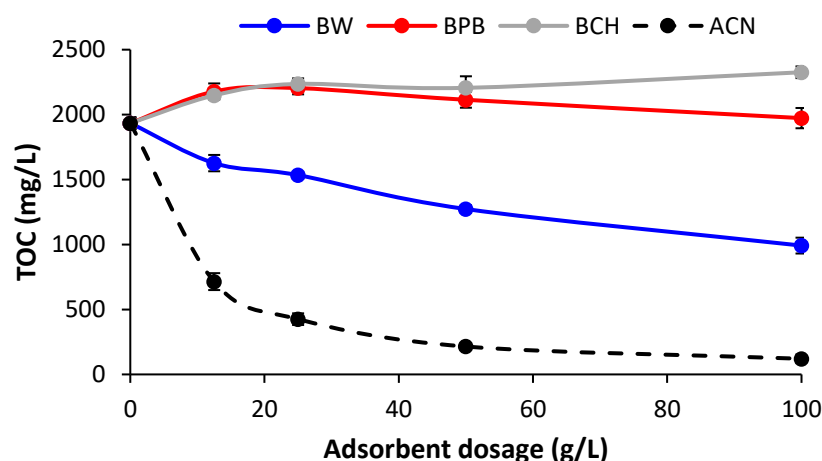


Figure 5. Removal of soluble organics (as TOC) from SWW at different adsorbent dosages ($n = 3$).

The initial TOC concentration in the SWW was 1934 mg/L, and this concentration was lower than that in the SHS used for soil washing (Table 1), indicating that some portion of the SHS (12%) was lost from solution during soil washing. On this basis, it can be assumed that the remaining fraction of soluble organics in the SWW consisted of soluble humic substances. Based on the methodology of SHS extraction, SHS contains macromolecular compounds such as humic and fulvic acids [16].

The TOC in the SWW decreased significantly when BW biochar and ACN were used, even at the lowest dosage (12.5 g/L). At a dosage of 100 g/L, the efficiencies of soluble organics removal with ACN and BW were 94% and 49%, respectively. The application of BCH increased the TOC concentration from 2148 mg/L (at 12.5 g/L) to 2326 mg/L (at 100 g/L). Similar trends were observed for BPB. This indicates that BCH and BPB biochars are not suitable for removing residual dissolved organics from the SWW. Although biochar is refractory, it can release dissolved organics, the amount and composition of which can vary greatly depending on the feedstock. The TOC for BW and ACN was 27 and 23 mg/L, respectively, while for BPB and BCH it was 120 and 132 mg/L, respectively. This could be an explanation for the increased TOC concentration in SWW treated with BPB and BCH.

The removal of dissolved organics from SWW may have been higher with ACN and BW than with the other adsorbents because of the mechanisms of organic removal with biochars. The first mechanism to consider is a pore-filling mechanism, in which the organics are at the surface of the biochar, which possesses mesopores (2–50 nm) and micropores (<2 nm) [50]. The presence of mesopores was shown to be crucial for the adsorption of humic acids onto biochar and activated carbon [56]. In the present study, ACN and BW had the best textural characteristics in terms of total pore volume and volumes of meso- and micropores (Table 2). In experiments with activated carbons and organics of different molecular weights and molecular sizes (phenol: 94 g/mol and 0.62 nm in diameter; iodine: 254 g/mol and 0.56 nm in diameter; tannic acid: 1701 g/mol and 1.6 nm in diameter), Hsieh and Teng [32] found that mesopores had a stronger effect on the capacity to adsorb larger adsorbates because mesopores reduced the length of the diffusion path of the micropores, and this length generally has a stronger effect on the diffusion of larger molecules than that of smaller molecules. According to Liu et al. [57], biochar prepared at 900 °C after modification with hydrochloric acid had a large specific surface area (459.3 m²/g) and a high porosity, and it removed over 80% of humic acids in aqueous solution at pH 5.0–9.0. Yan et al. [56] demonstrated that humic acids are better adsorbed on bamboo biochar than on helmpalm biochar and activated carbon. This is because bamboo biochar has a larger pore volume and wider pore size distribution and contains more polar functional groups on the surface, which makes it easier for it to bind humic acid than the other adsorbents.

It was shown that organics can also be adsorbed on the biochar surface through hydrophobic interaction. The removal took place via hydrophobic interaction due to the hydrophobic nature of the organics and the adsorbent [50]. In this study, ACN was the most condensed of the adsorbents (H:C ratio = 0.11, aromaticity of 63.4%at), which could have facilitated hydrophobic interactions with the hydrophobic parts of the humic substances from the SWW.

3.4. The Effect of Contact Time on the SWW Treatment

3.4.1. Heavy Metals

By investigating various contact times, it can be determined how long it takes an adsorbent to adsorb pollutants until adsorption equilibrium is reached. Figure 6 shows the effect of contact time between the adsorbents and the SWW on metal adsorption capacities. In general, the capacities of the different adsorbents to adsorb the metals decreased in this order: Zn > Pb > Cu > Ni > Cd. Only BCH had a higher capacity for adsorbing Pb than Zn during 180 min of adsorption (Figure 6c).

The adsorption process was fast, but its efficiency depended on the type of metal adsorbed on a given adsorbent. During the first 30 min of adsorption, the efficiency of metal adsorption was 72–99% with ACN, 29–85% with BW, 15–82% with BPB, and 6–76% with BCH. Pb was adsorbed most rapidly by all the adsorbents, with 76–99% of this metal adsorbed during the first 30 min of adsorption. During rapid adsorption, there are usually a large number of active sites on the adsorbent surface. Over time, more sites are occupied by heavy metal ions, and the rate of adsorption slows until equilibrium is reached [48].

The capacities for adsorbing the metals differed during the adsorption time. This is because metal removal depends not only on the adsorbent properties but also on the competition between pollutants, which is typical of mixed-pollutant solutions. In the present study, the SWW from soil washing contained heavy metals, alkaline ions, and soluble humic substances. Usually, the capacity for removal of a heavy metal is lower in a mixed solution than it is in a solution with a single solute, which might be due to faster saturation of the adsorption sites on biochar by mixed pollutants [48].

In the present study, adsorption equilibrium for all adsorbents and metals was reached at 180 min (Figure 6). Only in the case of Zn adsorption onto BPB was the adsorption capacity after 180 min about 30% lower than it was after 1440 min (Figure 6b). The literature indicates that the adsorption time required to achieve equilibrium adsorption of metals onto biochar varies widely, ranging from a few minutes to a few hours up to 24 h. Zhao

et al. [55] found that the time to reach equilibrium adsorption of multi-metals (Cr, Cd, Cu, and Pb) depended on the feedstock used for biochar preparation: 5 min with biochar from agricultural waste, 5 min to 24 h (depending on the metal) with wood biochar, and 8–24 h with sewage sludge biochar. Chen et al. [49] reported that Cu and Zn adsorption onto hardwood and corn straw was fast, with 77–83% of adsorption occurring during the first 120 min, followed by a very slow approach to equilibrium. Liu and Zhang [58] used biochars prepared from hydrothermal liquefaction of pinewood or rice husk and found that the contact time needed to reach 95% of the Pb removal equilibrium was less than 5 h with concentrations of 10–20 mg/L. Mohan et al. [59] used biochars made from oak wood, pine wood, oak bark, and pine bark and found that 40–70% of total Pb adsorption occurred within the first hour.

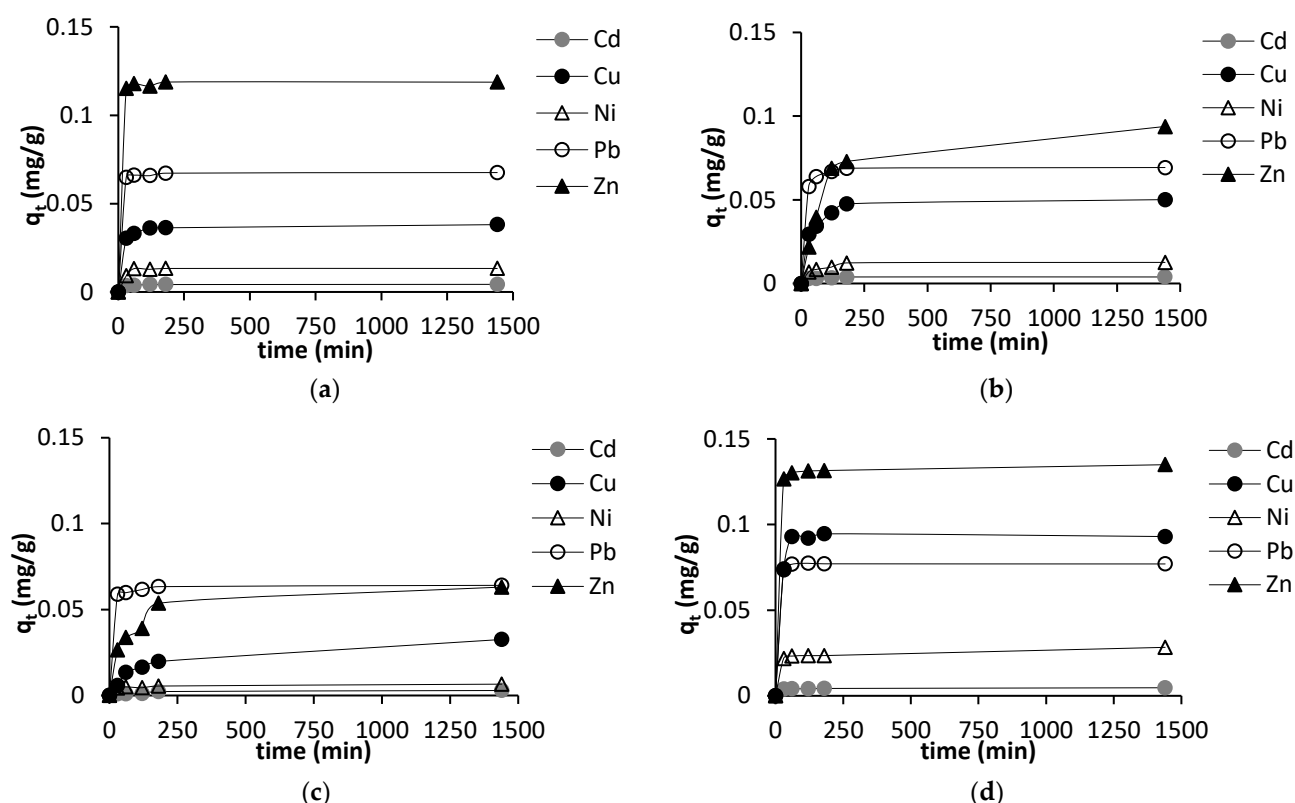


Figure 6. Effect of contact time on the metal adsorption capacities at different times (q_t) of the tested adsorbents: (a) BW, (b) BPB, (c) BCH, and (d) ACN.

For insight into the mechanisms of heavy metal adsorption onto the adsorbents, the data were analyzed with a pseudo-first-order kinetics model, a pseudo-second-order kinetics model, and an intraparticle diffusion model (Tables 5 and A3).

Pseudo-first-order kinetics are controlled by physical processes (e.g., weak van der Waals forces), while pseudo-second-order kinetics are controlled by chemical processes [55]. The high values of R^2 (from 0.96 to over 0.99) for these two kinetic models indicate that metal removal from SWW can be explained by these two processes. Other studies on the application of carbon-based adsorbents have also found that different kinetic models may describe the rate of adsorption of heavy metals equally well [60,61]. A pseudo-first-order model is appropriate for the initial contact time but not for the entire time [55].

Adsorption occurs rapidly due to the binding of metal ions to the biochar surface and is predominantly physical adsorption. Then the adsorption rate slows down, and chemisorption controls the adsorption process until equilibrium is reached. Additionally, at this stage, metal ions can diffuse into the macropores and micropores of the biochar and bind to the inner surface of the biochar to reach the adsorption endpoint [62,63]. The

rate-limiting steps in adsorption are external mass transfer (interfacial diffusion) and/or intraparticle diffusion [61].

Table 5. Parameters of pseudo-first-order and pseudo-second-order kinetics models of metal adsorption.

Adsorbent/ Metal		Pseudo-First Order			Pseudo-Second Order		
		k_1 1/min	q_e mg/g	R^2 -	k_2 g/(mg·min)	q_e mg/g	R^2 -
BW	Cd	0.0621	0.0042	0.9965	35.1408	0.0043	0.9992
	Cu	0.0553	0.0364	0.9962	3.2075	0.0382	0.9996
	Ni	0.0423	0.0133	0.9954	6.0823	0.0140	0.9874
	Pb	0.1189	0.0667	0.9997	12.4141	0.0673	0.9998
	Zn	0.1252	0.1179	0.9998	9.7425	0.1187	0.9998
BPB	Cd	0.0543	0.0036	0.9821	26.6563	0.0039	0.9920
	Cu	0.0257	0.0475	0.9877	0.7811	0.0516	0.9964
	Ni	0.0220	0.0120	0.9821	2.5908	0.0131	0.9912
	Pb	0.0621	0.0679	0.9987	2.2940	0.0704	0.9998
	Zn	0.0096	0.0934	0.9963	0.1217	0.1022	0.9897
BCH	Cd	0.0066	0.0029	0.9656	2.6020	0.0032	0.9631
	Cu	0.0063	0.0321	0.9879	0.2224	0.0352	0.9949
	Ni	0.0463	0.0055	0.9559	10.5117	0.0061	0.9755
	Pb	0.0943	0.0623	0.9984	5.5857	0.0637	0.9996
	Zn	0.0125	0.0603	0.9725	0.2860	0.0650	0.9878
ACN	Cd	0.0747	0.0043	0.9926	40.6366	0.0045	0.9966
	Cu	0.0536	0.0939	0.9990	1.4020	0.0972	0.9948
	Ni	0.0668	0.0248	0.9830	5.0726	0.0262	0.9903
	Pb	0.1028	0.0771	0.9999	8.6864	0.0778	0.9998
	Zn	0.1049	0.1321	0.9995	4.1552	0.1339	0.9999

The adsorbents had different structural properties that could have affected the diffusion process. Because the pseudo-first-order and pseudo-second-order kinetic models could not clearly identify the diffusion mechanism [64], the possibility of intra-particle diffusion was explored by using the intra-particle diffusion model. Figure A8 presents the plots of metal adsorption capacities versus $t^{0.5}$ for all the adsorbents. Two lines were fitted to the data, indicating that two steps influenced the adsorption process, and the kinetic parameters determined from the intraparticle diffusion model are shown in Table A3. The first straight line may reflect macropore and mesopore diffusion, and the second line may reflect micropore diffusion [65]. The increases in metal adsorption capacities were higher in the first phase than in the second one. Thus, the first stage had the strongest effect on the rate of adsorption. In the second phase, the diffusion of most metals remained limited due to the low metal concentrations [66,67]. The straight lines in the first phase showed deviation from the origin, which may be due to differences in the rate of mass transfer of a specific metal onto a given adsorbent. The values of C_i were higher than 0, indicating that intraparticle diffusion was not the main rate-limiting step of metal adsorption in this experiment, although it could have served to some extent as a co-mechanism.

Some film diffusion effects could have affected the adsorption of Cd and Cu on BCH biochar and the adsorption of Zn on BPB biochar, for which negative C_i values were obtained [68]. The BPB and BCH biochars had the smallest pore volumes, but their average pore diameter (128 nm) was in the macropore range. For adsorbents with a pore structure that consists of macropores, it is believed that the adsorbate undergoes film diffusion resistance not only on the outer surface of the adsorbent but also inside the large macropores (i.e., a film exists between the bulk of the pore and the inner pore surface) [68].

In general, the values of the intra-particle diffusion rate constants ($k_{i,1}$) were not high due to the relatively low metal concentrations in the SWW. The highest values were obtained for Zn and Cu, and the lowest for Cd. Usually, intraparticle diffusion has a faster adsorption rate at higher pollutant concentrations [69].

3.4.2. Soluble Organics (as TOC)

The effect of adsorption time was also shown in the removal of soluble organics from SWW (Figure 7). As shown, the removal of soluble organics (as TOC) during adsorption differed between the adsorbents. BCH biochar did not remove soluble organics. Their concentration during adsorption was higher than the concentration of organics in the SWW, increasing from 2104 mg/L (after 30 min) to 2326 mg/L (after 1440 min). These results suggest that BCH biochar is a source of soluble organics released under adsorption conditions. Similarly, with BPB biochar, the TOC concentration increased to 2142 mg/L within 180 min after adsorption. However, when the adsorption time was extended up to 1440 min, the organics released from the biochar were readsorbed, and the organics from the SWW were partially adsorbed, as the TOC concentration decreased to 1973 mg/L (Figure 7a). In contrast, BW and ACN were able to remove soluble organics from the SWW during the entire time of the experiment. The soluble organics were rapidly adsorbed by ACN and gradually by BW biochar. After 30 min, the TOC concentration in the SWW treated with ACN had decreased by 87%, and equilibrium was reached after 120 min (TOC removal efficiency of 91%). The use of BW biochar decreased the TOC concentration from 1874 mg/L (3% removal after 30 min) to 992 mg/L (49% removal after 1440 min), indicating that adsorption required more time than when using ACN. These results indicate that ACN was more effective than BW biochar for removing soluble organics from the SWW (Figure 7b).

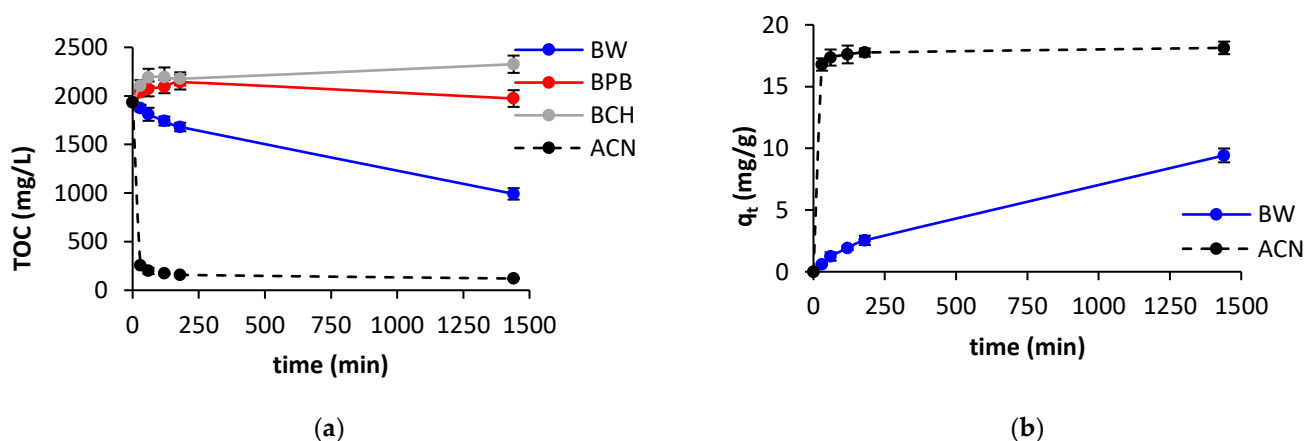


Figure 7. Effect of adsorption time on the concentration of soluble organics (as TOC) (a) and capacities for adsorption of soluble organics (b) (pH 4.88 with 100 g/L adsorbent) ($n = 3$).

Omri et al. [70] found that adsorption of humic acid onto almond shell activated carbon from aqueous solutions at different concentrations (10–100 mg/L) increased sharply in the first 180 min of contact time and that equilibrium adsorption was reached within 300 min. Yan et al. [56] observed that the capacities of bamboo biochar, helm palm biochar, and activated carbon to adsorb humic acid were highest during the first 4 h. The fast rate of adsorption at the beginning of the process was caused by humic acid adsorption on the exterior surface of activated carbon. After saturation of the exterior adsorption surface, humic acids can enter pores and are adsorbed by the interior surface [70].

Since only BW and ACN adsorbed soluble organics from SWW within the adsorption time, the kinetic models were fitted to the experimental data for only these two adsorbents to explore the mechanisms of soluble organic adsorption. The kinetic parameters of adsorption are listed in Table 6. All three kinetic models fit the data on the adsorption of soluble organics on BW and ACN well.

Table 6. Kinetic constants for soluble organics (as TOC) adsorption onto BW and ACN with different kinetic models.

Kinetic Model		BW	ACN
Pseudo-first order	k_1 (1/min)	0.0015	35.2196
	q_e (mg/g)	10.9698	17.7280
	R^2	0.9942	0.9987
Pseudo-second order	k_2 (g/mg·min)	0.0001	0.021
	q_e (mg/g)	14.0056	18.1490
	R^2	0.9855	1.0000
Intraparticle diffusion	Stage 1 _{30–180min}	k_i (mg/g·min ^{0.5})	0.2731 *
		C_i (mg/g)	−0.9825 *
		R^2	0.9982 *
	Stage 2 _{180–1440min}	k_i (mg/g·min ^{0.5})	−
		C_i (mg/g)	−
		R^2	−

* Values determined for adsorption time of 30–1440 min.

This indicates that the adsorption of soluble organics from the SWW, which had a very high initial concentration (1934 mg/L), was not determined by only one type of mechanism; instead, physical adsorption, chemisorption, and intraparticle diffusion were responsible for the removal of soluble organics (R^2 values for all three models were between 0.90 and 1.00). Many studies that have used carbon-based adsorbents to adsorb humic acids from aqueous solutions with concentrations up to 100 mg/L have indicated that the adsorption of humic acids appears to be controlled mainly by chemisorption processes [56,69,70].

In the present study, the adsorption rate constants (k_1 and k_2) from the pseudo-first and pseudo-second order models indicated that physical adsorption and chemisorption of soluble organics proceeded at a higher rate with ACN than with BW biochar. The faster and greater adsorption onto ACN is connected with the presence of a higher number of active sites on the surface of the adsorbent and the high probability of adhesion. This is because ACN has more pore structure and a greater specific surface area than BW biochar. These characteristics provide channels for adsorbate dispersion and improve mass transfer, which provide more active sites for the adsorption of soluble organics [57].

Adsorption data modeled with the intraparticle diffusion model usually indicate that there are two or three steps in the sorption process of different soluble organics [65]. According to the intraparticle model, the plot q_t against $t^{0.5}$ for BW biochar was linear over the entire adsorption time ($R^2 = 0.9982$, Figure A9a), revealing that only one stage was involved in the adsorption of soluble organics with this type of biochar. In this study, the plot of q_t against $t^{0.5}$ for BW did not pass through the origin, and the intercept (C_i) value was negative. This suggests that the adsorption of soluble organics could have been the result of the combined effects of film diffusion and adsorbent-surface interaction (chemical or physical interactions) [71]. The soluble organics were gradually adsorbed onto BW, but the final equilibrium adsorption stage was not reached. Thus, longer adsorption of soluble organics is needed to obtain equilibrium. Similarly, Zhu et al. [68] observed a time lag (hence a negative intercept, C_i) in the initial stage of the adsorption of pyridine onto synthetic polymers, which indicates that pyridine adsorption onto adsorbents experienced external film diffusion resistance.

In contrast, the plot q_t against $t^{0.5}$ for ACN was not linear over the whole range of time but was divided into two linear sections, implying that more than one process affected the adsorption of soluble organics, which is consistent with the higher efficiency of adsorption of these organic compounds with ACN. The pore diffusion rate constant decreased from 0.1555 (1st stage) to 0.0152 mg/g·min^{0.5} (2nd stage) (Table 6), indicating the diminishing role of intraparticle diffusion. Unlike adsorption with BW, the C_i was positive, indicating a lack of external film diffusion resistance during organic adsorption. Zhang [69] reported that the use of an intra-particle model indicated that the sorption of humic acid onto modified

biochar from forestry waste was also a multi-stage process. Three stages were indicated, each of which differed in the rate constants of intraparticle diffusion. The first stage was a fast process involving the transfer of the humic acid molecules from the main solution to the surface of the biochar. Due to the strong electrostatic attraction, it was interpreted as external surface adsorption or instantaneous adsorption. The second phase was interpreted as diffusion within the particles, as humic acid diffused into the pores or capillaries of the internal structure, which was referred to as mesopore diffusion and adsorption. The last phase was considered to be the final adsorption-desorption equilibrium, which is reached only after a long time. In the study by Zhang et al., equilibrium humic acid adsorption was reached between 60 and 750 min. In this study, equilibrium was reached after 180 min. of adsorption. Based on the C_i values, the rate-controlling mechanism of HA adsorption was mainly chemisorption but simultaneously affected by multiple mechanisms [69]. Other authors have confirmed that the sorption of soluble organics in the form of humic acids is not dominated by intraparticle diffusion [56]. Omri et al. [70] concluded that humic acid molecules are slowly transported via intraparticle diffusion into the particles of activated carbon and finally retained in their pores.

4. Conclusions

This study investigated soil washing with soluble humic substances combined with the treatment of generated wastewater (SWW) with biochar as an innovative and promising wastewater treatment technology. The SWW was characterized by a complex composition due to the presence of soluble organic matter (as humic substances), alkali elements (Na, Ca, Mg), and heavy metals (Cd, Cu, Ni, Pb, Zn). The differences in the physicochemical properties of the adsorbents affected their usability. All adsorbents had a positive effect on increasing the pH of SWW from acidic to slightly acidic and alkaline, as well as reducing salinity. Treatment of SWW required the use of high dosages of adsorbents in the range of 50–100 g/L. Activated carbon and willow biochar, which had the highest surface area, porosity, and pH and were more hydrophobic than other biochars, provided the best results in removing heavy metals and soluble organics from SWW.

The treatment of SWW was not determined by only one type of mechanism; instead, several mechanisms were involved. Analysis of the adsorption behavior of heavy metals and soluble organics with different kinetics models revealed that physical and chemical processes dominated, and diffusion into mesopores and micropores made lesser contributions. Depending on the type of adsorbent, the chemisorption of heavy metals was mainly determined by cation exchange, precipitation, complexation with functional groups and aromatic structures, and hydrophobic interactions with soluble organics.

Among the tested biochars, willow biochar was the most effective for the simultaneous removal of heavy metals and soluble organics from SWW. It is believed that willow biochar, after modification of its properties, has the potential to improve the treatment of SWW and be as effective as activated carbon. Using biochars made from a mixture of plant biomass or coconut husks in soil remediation could be considered for the recovery and reuse of soluble humic substances for further soil treatment by soil washing. Thus, the application of pyrolyzed biomass in soil washing to remove pollutants and/or recover washing agents can make this technology more sustainable.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

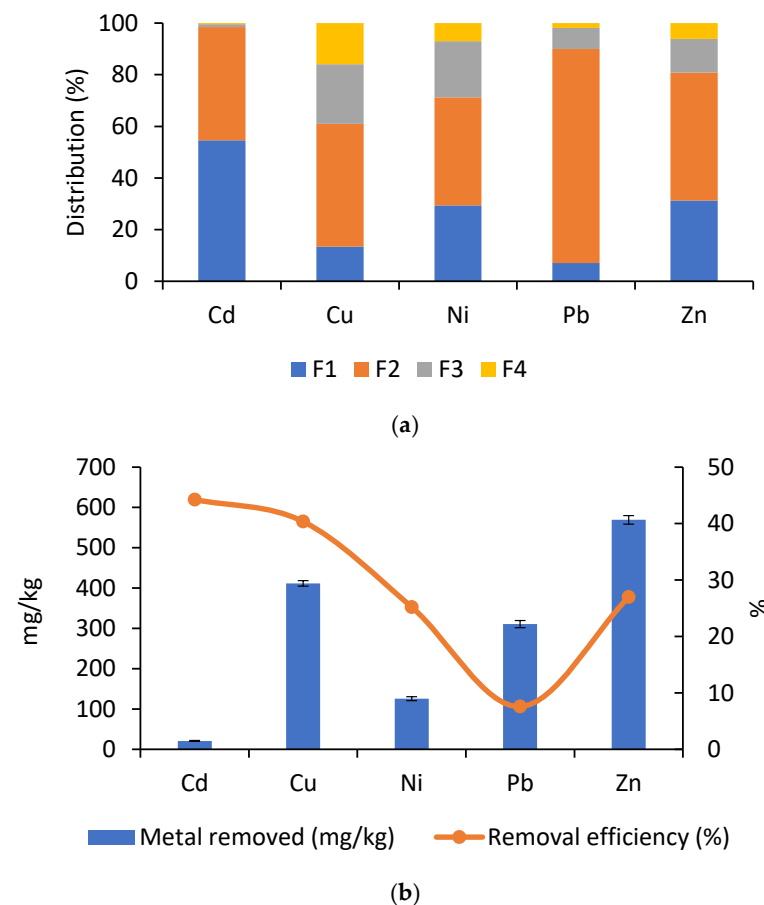


Figure A1. Metal distribution (a) and metal removal (b) from soil with SHS solution ($n = 3$). F1 is an exchangeable and acid-soluble fraction; F2 is a reducible fraction; F3 is an oxidizable fraction; and F4 is a residual fraction.

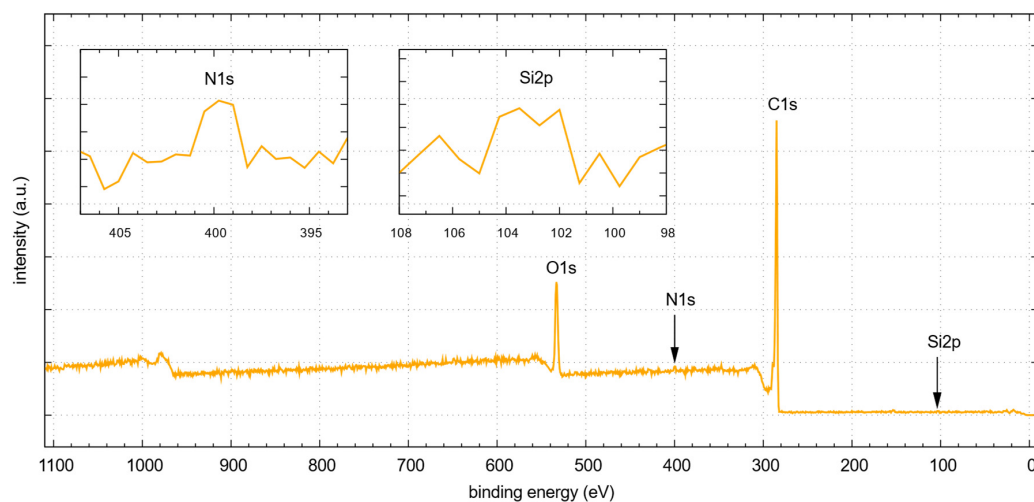


Figure A2. XPS survey spectrum of BW.

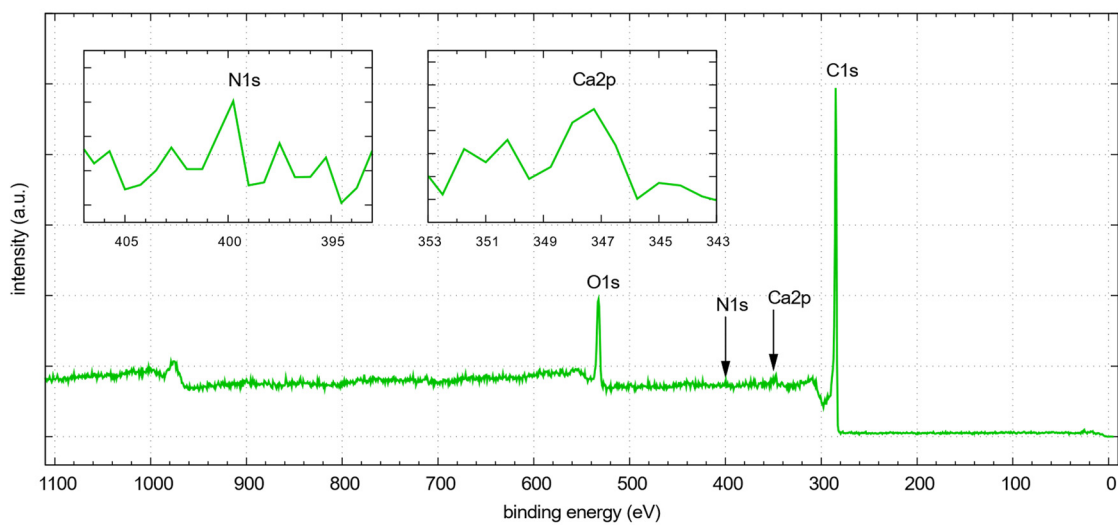


Figure A3. XPS survey spectra of BPB.

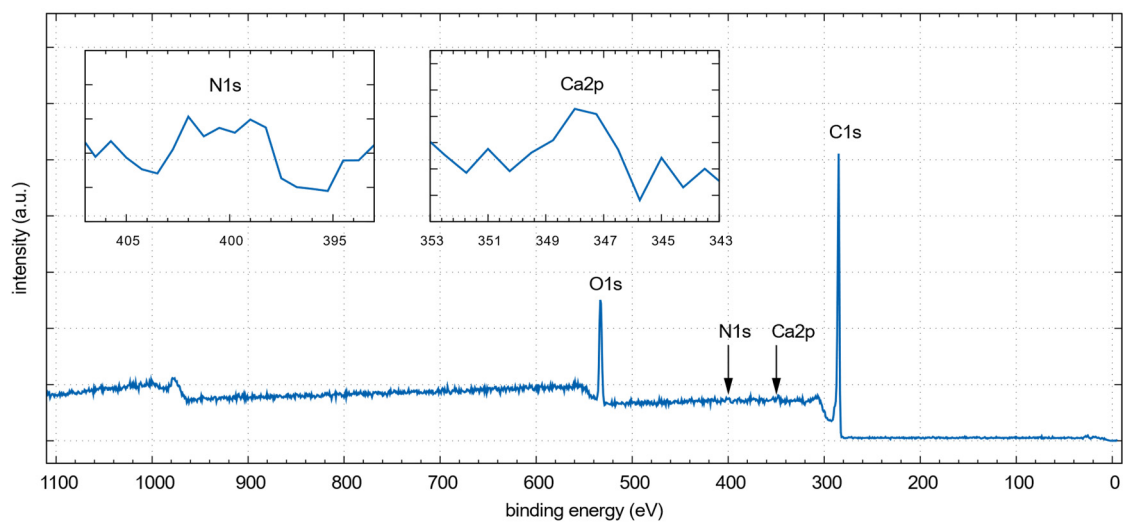


Figure A4. XPS survey spectrum of BCH.

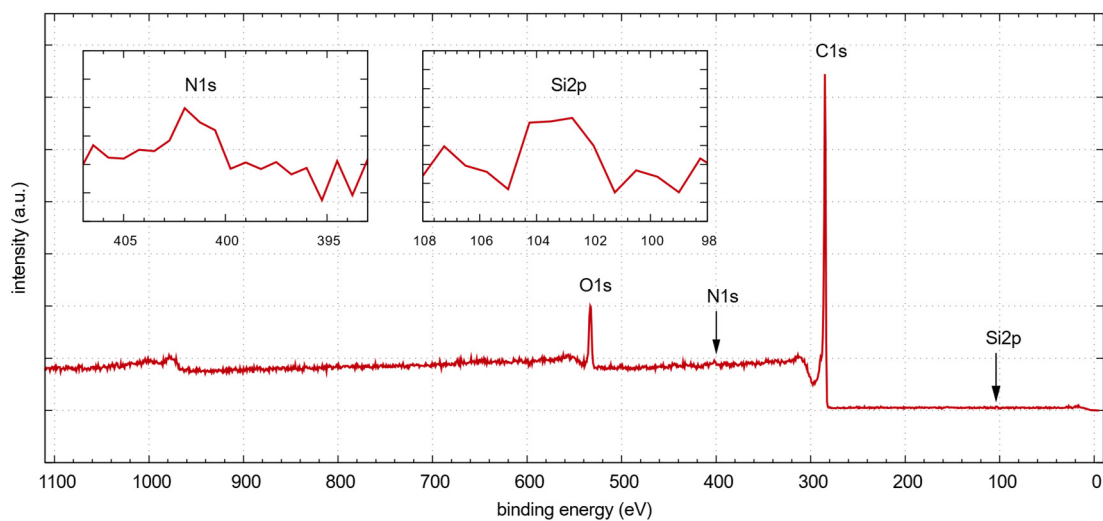


Figure A5. XPS survey spectrum of ACN.

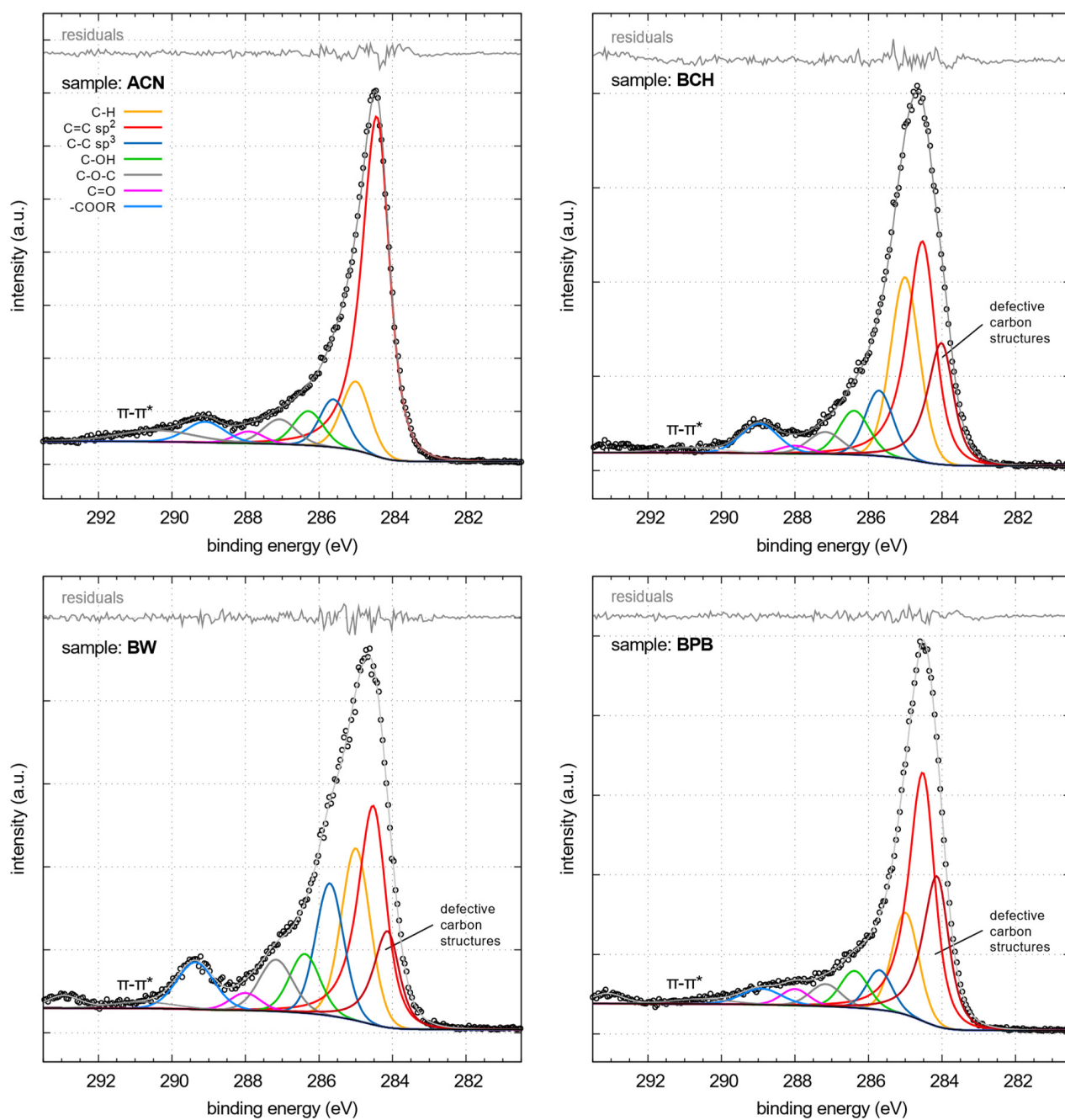


Figure A6. Fitting of XPS C1s spectra. Eight main components were used: C-H, C=C sp², C-C sp³, C-OH, C-O-C, C=O, -COOR, and π - π^* shake-up (i.e., bonding to antibonding transition). Details concerning these moieties and their binding energies are presented in table SI-T5 and in publications [72–74]. Additionally, for BCH, BW, and BPB samples, the component corresponding to defective carbon structures was added [75].

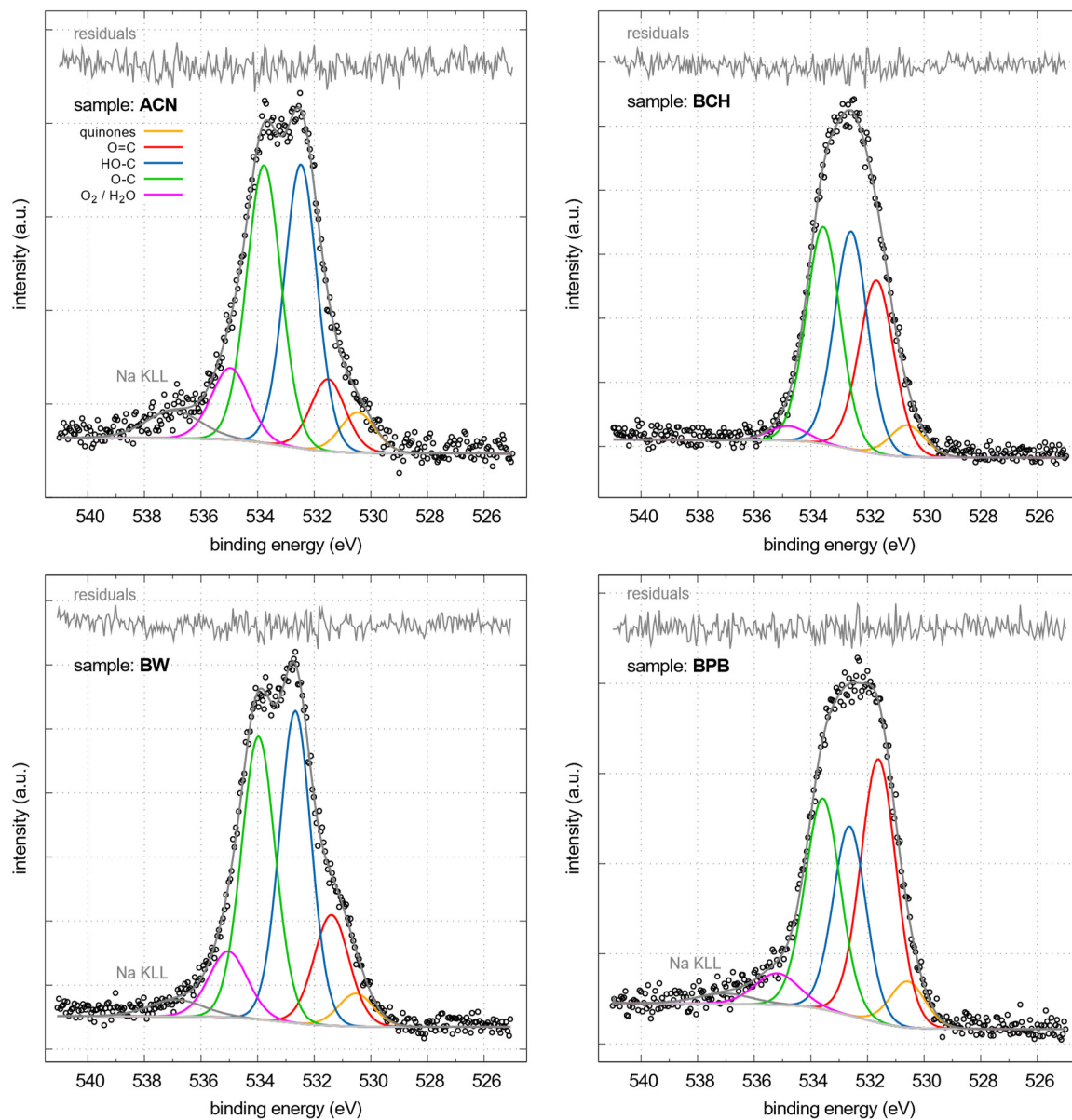


Figure A7. Fitting of XPS O1s spectra. Five peaks for the following components were used: quinones, carbonyl oxygen (O=C), hydroxyl groups (HO-C), oxygen single-bonded to carbon atoms (O-C, other than hydroxyls), and adsorbed molecular oxygen and/or water (O₂/H₂O). Details concerning their binding energies are given in table SI_T6 and publications [75–78].

Table A1. Fitting of XPS C1s spectra: surface atomic concentrations of components, their binding energies, and FWHMs. DCS stands for “defective carbon structures” [75].

Adsorbent	Name	Position	FWHM	%At Conc
BW	C-H	285.00	0.92	20.2
	C=C sp ²	284.51	0.83	29.1
	C-C sp ³	285.71	0.89	15.1
	C-OH	286.39	0.98	7.4
	C-O-C	287.17	1.08	7.1
	C=O	288.00	0.96	2.1
	-COOR	289.36	1.20	7.2

Table A1. *Cont.*

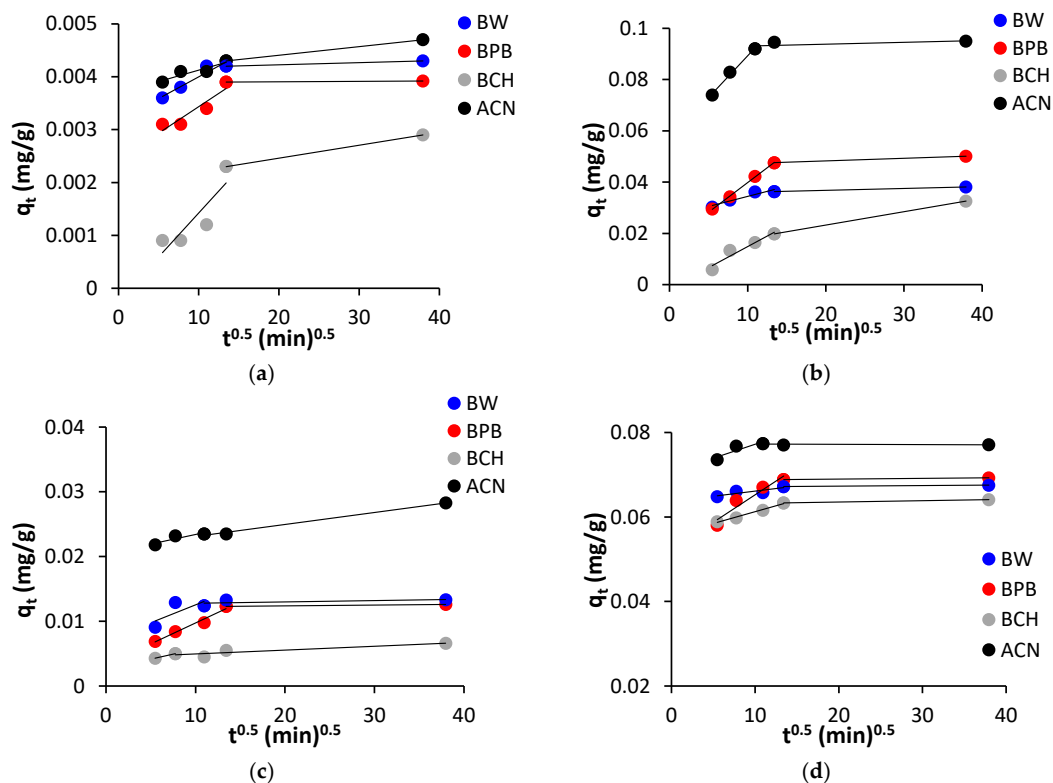
Adsorbent	Name	Position	FWHM	%At Conc
BPB	C–H	285.00	0.85	14.6
	C=C sp ²	284.51	0.76	40.3
	C–C sp ³	285.70	0.82	5.5
	C–OH	286.38	0.90	5.6
	C–O–C	287.17	0.99	3.7
	C=O	288.00	0.89	2.5
	–COOR	288.91	1.28	3.5
	DCS	284.13	0.76	24.3
BCH	DCS	284.13	0.76	11.8
	C=C sp ²	284.52	0.83	33.6
	C–C sp ³	285.71	0.89	8.6
	C–OH	286.39	0.97	6.3
	C–O–C	287.18	1.08	3.5
	C=O	288.01	0.96	1.1
	–COOR	288.97	1.19	5.2
	DCS	284.01	0.77	17.2
ACN	C–H	285.00	0.90	11.4
	C=C sp ²	284.42	0.81	63.4
	C–C sp ³	285.61	0.87	7.7
	C–OH	286.29	0.95	6.0
	C–O–C	287.07	1.05	4.8
	C=O	287.91	0.94	2.0
	–COOR	289.09	1.23	4.7

Table A2. Fitting of XPS O1s spectra: surface atomic concentrations of components, their binding energies, and FWHMs.

Adsorbent	Name	Position	FWHM	%At Conc
BW	quinones	530.52	1.44	4.2
	O=C	531.39	1.46	14.4
	HO–C	532.67	1.31	36.5
	O–C	533.97	1.41	35.4
	O ₂ /H ₂ O	535.04	1.61	9.5
BPB	quinones	530.58	1.46	6.2
	O=C	531.61	1.48	36.0
	HO–C	532.63	1.36	23.8
	O–C	533.58	1.47	28.7
	O ₂ /H ₂ O	535.20	1.83	5.3
BCH	quinones	530.59	1.45	4.9
	O=C	531.68	1.45	27.1
	HO–C	532.58	1.37	32.3
	O–C	533.56	1.41	33.1
	O ₂ /H ₂ O	534.81	1.59	2.5
ACN	quinones	530.46	1.45	5.5
	O=C	531.51	1.44	9.9
	HO–C	532.47	1.36	36.5
	O–C	533.78	1.43	37.5
	O ₂ /H ₂ O	534.97	1.56	10.6

Table A3. Parameters of the intraparticle diffusion model of metal adsorption.

Metal	Phase	Parameter	BW	BPB	BCH	ACN
Cd	1	$k_{i,1}$ (mg/g·min ^{0.5})	8×10^{-5}	0.0001	0.0002	4×10^{-5}
		$C_{i,1}$ (mg/g)	0.032	0.0024	−0.0002	0.0037
		R^2	0.9578	0.9297	0.8731	0.9270
	2	$k_{i,2}$ (mg/g·min ^{0.5})	4×10^{-6}	8×10^{-7}	2×10^{-5}	2×10^{-5}
		$C_{i,2}$ (mg/g)	0.0041	0.0039	0.002	0.0041
		R^2	1.0000	1.0000	1.0000	1.0000
Cu	1	$k_{i,1}$ (mg/g·min ^{0.5})	0.0008	0.0023	0.0016	0.003
		$C_{i,1}$ (mg/g)	0.0266	0.0167	−0.0016	0.0617
		R^2	0.9556	0.9995	0.9612	0.7872
	2	$k_{i,2}$ (mg/g·min ^{0.5})	7×10^{-5}	0.0001	0.0005	7×10^{-5}
		$C_{i,2}$ (mg/g)	0.0353	0.0931	0.0128	0.0924
		R^2	1.0000	1.0000	1.0000	0.6663
Ni	1	$k_{i,1}$ (mg/g·min ^{0.5})	0.0006	0.0006	0.0001	0.0003
		$C_{i,1}$ (mg/g)	0.007	0.0033	0.0038	0.0204
		R^2	0.7360	0.9855	1.0000	0.8977
	2	$k_{i,2}$ (mg/g·min ^{0.5})	2×10^{-5}	1×10^{-5}	4×10^{-5}	0.0002
		$C_{i,2}$ (mg/g)	0.0126	0.0121	0.0049	0.0213
		R^2	0.5853	1.0000	0.9111	0.9966
Pb	1	$k_{i,1}$ (mg/g·min ^{0.5})	0.0002	0.0013	0.0006	0.00007
		$C_{i,1}$ (mg/g)	0.0637	0.0522	0.0557	0.0706
		R^2	0.8727	0.9599	0.9942	0.8881
	2	$k_{i,2}$ (mg/g·min ^{0.5})	1×10^{-5}	2×10^{-5}	3×10^{-5}	-6×10^{-6}
		$C_{i,2}$ (mg/g)	0.067	0.0686	0.0629	0.0773
		R^2	1.0000	1.0000	1.0000	1.000
Zn	1	$k_{i,1}$ (mg/g·min ^{0.5})	0.0003	0.0068	0.0032	0.0008
		$C_{i,1}$ (mg/g)	0.114	−0.0132	0.0083	0.1227
		R^2	0.7261	0.9746	0.9663	0.9193
	2	$k_{i,2}$ (mg/g·min ^{0.5})	4×10^{-7}	0.0009	0.0004	0.0001
		$C_{i,2}$ (mg/g)	0.1188	0.0615	0.0485	0.1297
		R^2	1.0000	1.0000	1.0000	0.9999

**Figure A8.** Cont.

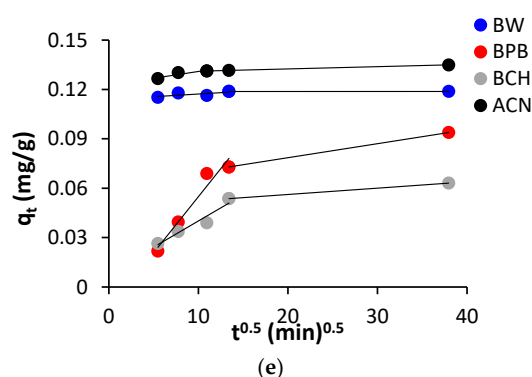


Figure A8. Kinetics of metal adsorption according to the intraparticle diffusion model: (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn. The first line refers to phase 1, while the second line refers to phase 2.

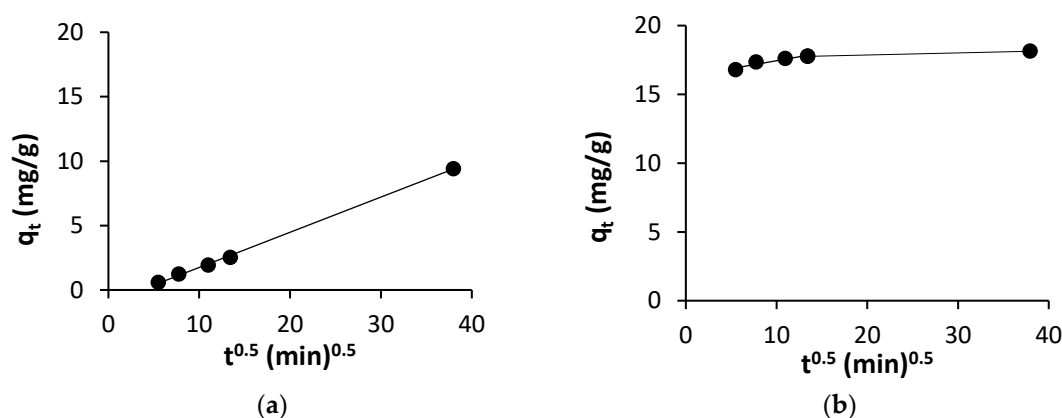


Figure A9. Kinetics of soluble organics (as TOC) adsorption according to the intraparticle diffusion model: (a) BW and (b) ACN. The first line refers to phase 1, while the second line refers to phase 2.

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