

Article

Thermal Conversion of *Paulownia tomentosa* Leaves into Carbonaceous Materials: Effects on Physicochemical Properties and Sorption of Metribuzin and Tebuconazole from Water

Margita Ščasná¹ , Michal Hebnár¹, Alexandra Kucmanová¹ , Maroš Sirotiak¹ , Veronika Kvorková¹ , Maroš Soldán¹, Jan Hajzler² , Barbora Ludrovčová³  and Marián Palcut^{4,*} 

¹ Institute of Integrated Safety, Faculty of Materials Science and Technology, Slovak University of Technology, J. Bottu 25, 917 24 Trnava, Slovakia; margita.scasna@stuba.sk (M.Š.); xhebnar@stuba.sk (M.H.); alexandra.kucmanova@stuba.sk (A.K.); maros.sirotiak@stuba.sk (M.S.); veronika.kvorkova@stuba.sk (V.K.); maros.soldan@stuba.sk (M.S.)

² Materials Research Center, Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, 612 00 Brno, Czech Republic; jan.hajzler@vut.cz

³ Institute of Production Technologies, Faculty of Materials Science and Technology, Slovak University of Technology, J. Bottu 25, 917 24 Trnava, Slovakia; barbora.ludrovцова@stuba.sk

⁴ Institute of Materials Science, Faculty of Materials Science and Technology, Slovak University of Technology, J. Bottu 25, 917 24 Trnava, Slovakia

* Correspondence: marian.palcut@stuba.sk

Abstract

This study investigated carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization, slow pyrolysis, and HCl post-treatment for the adsorption of metribuzin and tebuconazole from water. Hydrochars were prepared at 180–220 °C, pyrochars at 400–600 °C, and the pyrochar produced at 600 °C was further treated with HCl. The materials were characterized by yield, ash content, active and exchangeable pH, oxidizable organic carbon content, FTIR, SEM, and CO₂-derived surface and pore properties. Increasing processing temperature reduced the yield in both conversion routes. Hydrochars retained more oxygen-containing and oxidizable organic structures, whereas pyrochars showed stronger carbonization, higher ash content, and higher CO₂-derived surface area. HCl treatment decreased the ash residue, thereby resulting in improved CO₂-accessible surface and pore properties and more fragmented morphology. Metribuzin adsorption was better described by the pseudo-second-order kinetic model across all sorbents, with the highest fitted equilibrium adsorbed amount observed following HCl treatment. Tebuconazole showed higher initial uptake toward most untreated materials, but its kinetic profiles were non-monotonic, with a decrease in the adsorbed amount at longer contact times. Consequently, the conventional PFO and PSO models did not adequately describe its complete kinetic behavior. Nonlinear isotherm modeling showed predominantly Freundlich-type fitting for metribuzin, suggesting heterogeneous adsorption sites, whereas tebuconazole was formally better described by Langmuir-type fitting, although with poorer fit quality for several materials. The results show that *Paulownia tomentosa* leaves are a suitable precursor for carbonaceous sorbents and that HCl-treated pyrochar is the most promising material for metribuzin adsorption.

Keywords: acid washing; DFT pore analysis; hydrothermal carbonization; pesticide-contaminated water; slow pyrolysis



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1. Introduction

Thermochemical conversion of biomass is a useful technique for valorizing plant residues and other organic waste into value-added materials [1]. Biomass may undergo a range of technological treatments, for example, hydrothermal carbonization, pyrolysis, torrefaction, or gasification, each of which results in a different product distribution and different properties of the solid carbon fraction [2–4]. Among these approaches, hydrothermal carbonization and slow pyrolysis were selected for this study, as they enable the preparation of carbonaceous materials with markedly different surface chemistries and pore structures, thus providing a suitable basis for evaluating the influence of the properties of the conversion route on the resulting material [5,6].

The properties of the prepared carbonaceous materials are given not only by the type of input biomass, but also by the processing temperature and any subsequent treatment. Increasing the pyrolysis temperature is generally associated with a more intense release of volatile components [7,8], increased porosity and expansion of specific surface area [9]. In contrast, under milder conditions, hydrochar typically retains a larger fraction of oxygen-bearing functional groups [10,11] and a different surface chemical character [12,13]. For this reason, hydrochar and pyrochar cannot be considered interchangeable materials; rather, comparing them using the same precursor provides valuable information on how the technological route influences yield, ash content, acid-base properties, texture, and surface chemical composition [12,14,15].

Post-synthesis treatment is also an important step in the design of carbon-based materials. Biochar post-treatment is used to tailor surface properties and improve performance in aquatic environments [16–18]. Common approaches include acid washing or acid-base treatment [19], metal impregnation [20], composite preparation [21,22], or mechanical treatment [23]. Acid washing generally serves two main functions: it removes mineral and ash-forming impurities while altering the nature of surface functional groups [19,24]. In the case of hydrochloric acid treatment, changes in acid-base properties, a reduction in the proportion of the inorganic fraction, and changes in the availability of active sites can be expected, which may subsequently manifest in the material interaction with pollutants in water.

Carbon-based materials derived from biomass have been extensively studied in recent years as low-cost sorbents for water treatment. Their advantages include relatively simple preparation, the wide availability of raw materials, and the ability to tailor their properties by selecting the precursor, carbonization conditions, or subsequent post-treatment [25,26]. Special attention should be given to the removal of pesticides, as these compounds enter the aquatic environment through agricultural runoff, leaching, and improper handling, and can persist in both surface and groundwater [27,28]. More soluble pesticides are more easily transported in aquatic environments, while less soluble compounds can bind to solid particles and be transported by erosion and runoff [29]. Metribuzin and tebuconazole are two pesticide active ingredients with distinct physicochemical properties, making them suitable model contaminants for comparing their interactions with prepared carbonaceous materials. Metribuzin is characterized by high water solubility (1050–1220 mg/L) and low log K_{ow} (1.6–1.7) [30,31], whereas tebuconazole shows much lower water solubility (36–38 mg/L) and a higher log K_{ow} (3.1–3.7) [32], indicating a more hydrophobic character [33–35]. These differences are relevant for adsorption because metribuzin may interact more strongly with polar oxygen-containing surface groups, whereas tebuconazole may show stronger affinity toward carbon-rich and aromatic domains through hydrophobic and π - π interactions.

Paulownia tomentosa leaves represent a suitable and still insufficiently explored precursor for the preparation of carbonaceous sorbents. *Paulownia* is a fast-growing tree species

that produces a considerable amount of leaf biomass, which is often treated as low-value plant residue. The valorization of this residual biomass through thermochemical conversion is therefore consistent with the principles of waste utilization and material recovery. To date, studies on carbonaceous materials derived specifically from *Paulownia tomentosa* leaves remain scarce. Available work has focused mainly on hydrochars and modified hydrochars prepared from *Paulownia* leaves, particularly for the removal of inorganic contaminants such as Pb^{2+} from aqueous solutions [36–38]. However, a systematic comparison of hydrochar, pyrochar, and acid-washed pyrochar prepared from the same *Paulownia tomentosa* leaf precursor, together with their application for pesticide adsorption, has not yet been sufficiently addressed.

The study aimed to prepare carbonaceous materials from *Paulownia tomentosa* leaves using hydrothermal carbonization, slow pyrolysis, and subsequent acid treatment of selected pyrochar. The effects of the conversion route, processing temperature, and HCl post-treatment on yield, ash content, active and exchangeable pH, surface functional groups, oxidizable carbon content, morphology, and textural properties were systematically evaluated. The functionality of the prepared materials was assessed by sorption experiments with metribuzin and tebuconazole in aqueous media, using kinetic and isotherm analyses.

The working hypothesis was that the conversion route, processing temperature, and HCl washing would modify the physical and chemical properties and thereby affect the sorption behavior of the prepared carbonaceous materials toward the target pesticides.

2. Materials and Methods

The following abbreviations are used throughout the manuscript: HCH denotes hydrochar prepared by hydrothermal carbonization, PCH denotes pyrochar prepared by slow pyrolysis, and PCH 600 HCl denotes pyrochar prepared at 600 °C and subsequently treated with hydrochloric acid. The numbers in the sample labels indicate the processing temperature in °C. MB and TB denote metribuzin and tebuconazole, respectively.

Analytical-grade chemicals were purchased from MERCK Ltd. (a subsidiary of Merck KGaA, Darmstadt, Germany) and FISHER Slovakia, Ltd. (a subsidiary of Thermo Fisher Scientific Inc., Waltham, MA, USA), and HPLC-grade solvents from VWR International, Ltd. (Bratislava, Slovakia).

2.1. Production of Carbonaceous Materials by Thermochemical Techniques

Hydrochar was prepared in a PPL100 hydrothermal reactor constructed from 304 stainless steel with a polytetrafluoroethylene (PPL) lining (Tefic Biotech, Xi'an, China). The reaction mixture consisted of 5.00 g of dried and ground *Paulownia tomentosa* leaf biomass dispersed in 60 mL of deionized water. This precursor-to-water ratio was selected based on preliminary hydrothermal carbonization trials. At lower biomass loading, the suspension was too diluted and the formation of a separable solid hydrochar phase was less effective, with a larger proportion of carbonaceous products remaining dispersed or dissolved in the liquid phase. In contrast, higher biomass loading resulted in an overly dense suspension and the formation of a compact, gel-like solid phase, which was difficult to homogenize, wash and separate after treatment. Therefore, the selected ratio represented a practical compromise that ensured sufficient wetting and homogenization of the precursor, effective solid-phase formation, and good post-treatment handling of the hydrochar.

The suspension was homogenized by mechanical shaking for 5 min before sealing. After sealing, the PPL liner was inserted into the steel outer jacket, and the entire reactor was transferred and positioned in a programmable oven. Heating to the designated temperatures of 180, 200, and 220 °C proceeded at a controlled heating rate of 5 °C/min, followed by a one-hour holding time.

After the reaction was completed, the autoclave was allowed to cool naturally to laboratory temperature. The resulting suspension was separated by centrifugation (Compact Star CS8, Avantor, VWR International, Stříbrná Skalice, Czech Republic) at 5000 rpm ($3070 \times g$) for 10 min. The solid hydrochar was repeatedly washed with deionized water and then dried in a Memmert drying cabinet (Memmert GmbH + Co. KG, Schwabach, Germany) at 105 °C until constant weight was obtained (24 h). The dried hydrochar was mechanically homogenized (milled in a blade mill, then sieved through a laboratory mesh to obtain a fraction under 100 μm) and then stored in a desiccator over silica gel prior to its experimental application.

Pyrochar was prepared in the LAC LE05/11 laboratory furnace (LAC, Ltd., Židlochovice, Czech Republic) by slow pyrolysis. The reaction mixture consisted of 5 g of ground dried biomass of *Paulownia tomentosa* leaves placed in 3/60 porous porcelain crucibles. Pyrolysis was conducted in flowing N_2 (20 mL/min). The heating to target temperatures of 400 °C, 500 °C, and 600 °C was carried out at a 10 °C/min heating rate, followed by a 60 min hold.

When the reaction was complete, the crucibles were allowed to cool in a desiccator to the stable laboratory temperature. Pyrochar was homogenized in the same way as hydrochar and stored in a desiccator until further application in the following experiments.

2.2. Post-Treatment of Pyrochar at 600 °C with HCl

The pyrochar prepared at 600 °C was subsequently subjected to acid treatment to remove ash-forming and mineral components. In this procedure, 2.50 g of pyrochar was weighed into 100 mL vessels. Subsequently, 50 mL of HCl (1 mol L^{-1}) was added, yielding a 1:20 g:mL solid-to-liquid ratio [39]. The reaction mixture was agitated [40] with a back-and-forth shaker (Heidolph Promax 1020) for 2 h at 200 rpm speed. After acid treatment, the sample was repeatedly rinsed with Milli-Q water until reaching a neutral pH. The treated material was then dried in a laboratory oven at 105 °C to a constant mass for 24 h. The resulting pyrochar was kept in a desiccator until further use.

2.3. Physicochemical and Structural Characterization of Carbonaceous Materials

The active and exchangeable pH values of the prepared carbonaceous materials were determined using a Multi 340i pH meter equipped with a SenTix 41 electrode (WTW GmbH, Xylem Analytics, Weilheim, Germany). Active pH was determined in an aqueous suspension and reflects the acid-base behavior of the material in water. Exchangeable pH was determined in a 1 mol/L KCl solution, where K^+ ions can replace exchangeable acidic ions associated with the surface of the solid material, thereby providing information on its exchangeable acidity. Therefore, exchangeable pH may be lower than active pH and provides additional information on the exchangeable acidity of the material.

For active pH measurement, samples with particle size < 100 μm were suspended in high-purity water (electrical conductivity < 0.2 $\mu\text{S}/\text{cm}$) at a weight-to-volume ratio of 1:10. Exchangeable pH was measured in 1 mol/L KCl solution at the same weight-to-volume ratio. After stirring for 60 min on a magnetic stirrer, both suspensions were allowed to stand for 10 min, and their pH was then measured [40,41].

The yield of the carbonaceous material was calculated as the mass ratio of the dry solid product to the initial biomass dry weight and expressed as a percentage (%). The samples were dried to constant weight before weighing. Weights were determined using RADWAG AS 310/C/2 analytical balances (scale precision 0.1 mg, Radom, Poland). Each determination was performed in three independent replicates for all prepared samples.

The ash content was determined gravimetrically in five independent replicates, as described in [42]. An aliquot of about 1 g of the dried sample was placed on an analytical

scale in a covered crucible and weighed, and subsequently inserted into a LAC LE05/11 furnace with an Ht60B controller. The temperature was increased gradually to 250 °C and held for 60 min. Afterward, the temperature was elevated to 550 °C and held for two h. After annealing, the crucible was moved to a desiccator and allowed to cool down to laboratory temperature. Once cooled, the crucible with ash was placed on a balance and weighed. The ash content was calculated and given in wt.% (*w/w*).

The content of oxidizable organic carbon (C_{oxi}) in the solid samples was quantified spectrophotometrically using an Agilent Cary 60 instrument (Agilent Technologies, Santa Clara, CA, USA) at 590 nm. The modified Turin method [43] was utilized, based on the oxidation of organic carbon by K_2CrO_4 in a concentrated H_2SO_4 solution. During the reaction, hexavalent cation (Cr^{6+}) is reduced to trivalent chromium (Cr^{3+}). C_{oxi} in the material is proportional to the amount of Cr^{3+} formed. The determination was performed in three independent replicates for all analyzed samples, including biomass and prepared biochar. The C_{oxi} results are given as mean $\pm$ standard deviation.

Surface functional groups of carbonaceous materials were analyzed by FTIR using a Varian 660 MidIR spectrophotometer with a GladiATR accessory with a diamond crystal and dual MCT/DTGS detectors (Varian, Palo Alto, CA, USA). Spectra were collected in a 500–4000 cm^{-1} range over 256 scans, and processed using Varian Resolutions Pro software version 5.1.0.829. Subsequent processing and visualization of spectral data, including vertical shifting of spectral curves (stacked spectra), were performed using Origin 9.1 software (OriginLab Corporation, Northampton, MA, USA).

The morphological features of the samples were studied using a scanning electron microscope (JEOL JSM-7600F, SEM). The microscope was operated at 1.0 kV accelerating voltage and 15 mm working distance. The surface topography was visualized in a secondary electron imaging mode at different magnifications.

The surface and pore properties of the prepared materials were investigated using a NOVA 2200e surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL, USA) based on CO_2 adsorption isotherms acquired at 273 K. Prior to analysis, all samples were degassed under vacuum at 120 °C for 24 h to remove adsorbed moisture and residual volatile species. CO_2 was selected as the adsorptive gas because the prepared carbonaceous materials were expected to contain a substantial fraction of narrow micropores and ultramicropores. Compared with N_2 adsorption at 77 K, CO_2 adsorption at 273 K provides improved diffusion into narrow micropores and is therefore suitable for evaluating the CO_2 -accessible microporous structure of carbonaceous materials. This approach is consistent with previous studies on porous carbons, where CO_2 adsorption at 273 K was shown to be particularly useful for characterizing narrow microporosity and overcoming diffusion limitations associated with N_2 adsorption in ultramicroporous structures [44].

The pore structure parameters were evaluated using density functional theory (DFT) implemented in NovaWin software (v. 11.06). The DFT approach was used to determine the specific surface area, pore volume, and dominant pore width from the experimental CO_2 adsorption data. All measurements were performed in triplicate.

It should be noted that CO_2 adsorption at 273 K mainly characterizes the microporous and ultramicroporous domains accessible to CO_2 molecules and does not provide a complete description of mesopores and macropores. Therefore, the obtained textural parameters are discussed in terms of CO_2 -accessible surface and pore properties.

2.4. Adsorption Kinetics and Isotherm Equations

Batch adsorption experiments were done for metribuzin and tebuconazole under controlled laboratory conditions at 25 ± 1 °C. For kinetic measurements, 0.025 g of sorbent

was placed into 10 mL glass vials and mixed with 5.0 mL of pesticide solution (30 mg/L initial concentration). The vials were sealed and shaken at 20 rpm using a Roto-Therm™ Plus Incubated Rotator H2024 (Benchmark Scientific, Sayreville, NJ, USA). The contact time ranged from 0 to 1440 min, and samples were collected at predetermined intervals.

The adsorption isotherms were determined under identical conditions using 0.025 g of sorbent and 5.0 mL of pesticide solution with different initial concentrations. Metribuzin was tested at seven initial concentrations ranging from 5 to 100 mg/L, while tebuconazole was tested at seven initial concentrations ranging from 5 to 35 mg/L. The mixtures were constantly shaken over 24 h to attain equilibrium. The pH was monitored in a separate parallel sample at the beginning, in the middle, and at the end of the experiment. The pH remained close to neutral, and its variation did not exceed ± 0.5 pH units during the adsorption experiments.

After adsorption, the liquid and solid phases were sedimented by centrifugation for 5 min at 1200 rpm using a laboratory centrifuge (Compact Star CS8 Avantor, VWR International, Stříbrná Skalice, Czech Republic). The supernatant was carefully removed, filtered, and analyzed for residual pesticides using HPLC-UV. All experiments were performed in triplicate. Blank pesticide solutions without sorbent were included to verify pesticide stability and to assess potential losses due to contact with glassware or during filtration. In addition, sorbent blanks without pesticide were prepared under the same experimental conditions to check whether compounds released from the sorbents interfered with HPLC-UV detection at the analytical wavelengths used for metribuzin and tebuconazole. No relevant interference was observed. All samples, including blanks and initial-concentration controls, were filtered through the same PTFE filters to ensure uniform sample treatment. Adsorption losses on glassware were considered negligible.

The amount of adsorbed pesticide at time t , q_t (mg/g), is given by Equation (1) [45]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

In Equation (1), the symbol C_0 (mg/L) is used to mark the initial concentration, C_t (mg/L) represents the concentration at time t , V (L) represents the solution volume, and m (g) is the sorbent weight.

For adsorption isotherms, q_e (mg/g) represents the equilibrium adsorbed amount at a given equilibrium concentration. It is expressed by Equation (2):

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

In Equation (2), the symbol C_e represents the pesticide equilibrium concentration in mg/L.

The kinetic results were analyzed using nonlinear forms of pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The models are expressed as [46–48]

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

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

In Equations (3) and (4), q_e represents the equilibrium adsorbed amount in mg/g, k_1 is the PFO rate constant in min^{-1} , and k_2 is the PSO rate constant in $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$.

Equilibrium adsorption results were evaluated using nonlinear forms of the Langmuir model and the Freundlich equation. The Langmuir model describes monolayer adsorption

on a surface with energetically equivalent adsorption sites. It was applied in the following nonlinear form [49]:

$$q_e = \frac{q_{max} \times K_L \times C_e}{1 + K_L \times C_e} \quad (5)$$

In Equation (5), the symbol K_L is used to represent the Langmuir constant (L/mg), and q_{max} (mg/g) is used to represent the maximum adsorption capacity.

The Freundlich equation was used to describe adsorption on a heterogeneous surface. It was applied in the following nonlinear form [50]:

$$q_e = K_F \times C_e^{1/n} \quad (6)$$

In Equation (6), n is the heterogeneity factor, and the symbol K_F is used for the Freundlich constant. The unit of K_F depends on the value of $1/n$, while n is dimensionless.

Kinetic parameters were obtained by nonlinear regression of the kinetic data, while isotherm parameters were obtained by nonlinear regression of the equilibrium q_e - C_e data. The fitting was performed using the least-squares method in the original q_t - t and q_e - C_e spaces. The sum of squared errors, SSE, was used to evaluate the goodness of fit. SSE is given by the following equation [47,51]:

$$SSE = \sum (q_{exp} - q_{calc})^2 \quad (7)$$

In Equation (7), q_{calc} and q_{exp} represent the calculated and experimental adsorbed amounts, respectively. The model or equation with the lower SSE value was considered to provide a better fit. In addition, the coefficient of determination, R^2 , was used to support the evaluation of the fit. For adsorption isotherms, the better-fitting isotherm was selected based on a higher R^2 value and a lower SSE value [52–54].

2.5. HPLC-UV Analysis of Metribuzin and Tebuconazole

High-performance liquid chromatography (HPLC) was used to determine the metribuzin concentration, following a procedure given in [55]. The separation was carried out on an Agilent InfinityLab Poroshell 120 Eclipse EC-C18 reverse-phase column (4 μ m, 4.6 $\times$ 150 mm; Agilent Technologies, Santa Clara, CA, USA) at isocratic conditions by using a mobile phase of ultrapure H_2O and CH_3CN at a volume ratio of 50:50. The mobile phase flow rate was 1.0 mL/min. The column temperature of 50 $^{\circ}C$ and injection volume of 10 μ L were used. The detection was carried out at a 254 nm wavelength.

Tebuconazole determination was performed using the same HPLC-UV technique, following the procedure described in [35]. The analysis was carried out on the same C18 column under isocratic conditions with CH_3CN - H_2O mobile phase (65:35, v/v). The mobile phase flow rate was 1.0 mL/min, and the injection volume was 10 μ L. The detection was done at 220 nm, and the column temperature was 30 $^{\circ}C$.

The methods were developed and validated in previous studies in accordance with ICH Q2(R1) guidelines [56], with linearity, precision, accuracy, limit of detection (LOD), and limit of quantification (LOQ) verified. No significant interference was observed within the retention time range of the analytes of interest during the analyses.

2.6. Statistical Analysis

Statistical analysis was used to directly measure physicochemical parameters obtained from independent replicates, specifically ash content and oxidizable organic carbon content. ANOVA, i.e., one-way analysis of variance, followed by Tukey's post hoc test, was used to reveal significant differences among samples at $p < 0.05$. Homogeneity of variance was checked prior to ANOVA. Statistical analyses were performed using OriginPro 9.1.

The statistical evaluation followed standard approaches for measured datasets, including hypothesis testing and assessment of basic statistical parameters such as mean and variance [57].

3. Results and Discussion

3.1. Influence of Conversion Route and Temperature on Yield and Ash Content

The carbonaceous materials yield was found to decrease with increasing processing temperature for both conversion routes (Figure 1, Table S1). Hydrochar yield decreased from 51.68% at 180 °C to 42.50% at 220 °C, which is consistent with the progressive decomposition of cellulosic and hemicellulosic fractions under HTC conditions [58–60]. On the contrary, pyrochar exhibited substantially higher yields over the studied temperature range, decreasing from 74.98% at 400 °C to 60.17% at 600 °C [60–62]. The lower yields observed for hydrochar can be attributed to hydrolysis and partial solubilization of lignocellulosic fraction in subcritical water, whereas mass loss during pyrolysis is driven mainly by devolatilization and thermal depolymerization under dry inert conditions [63–66].

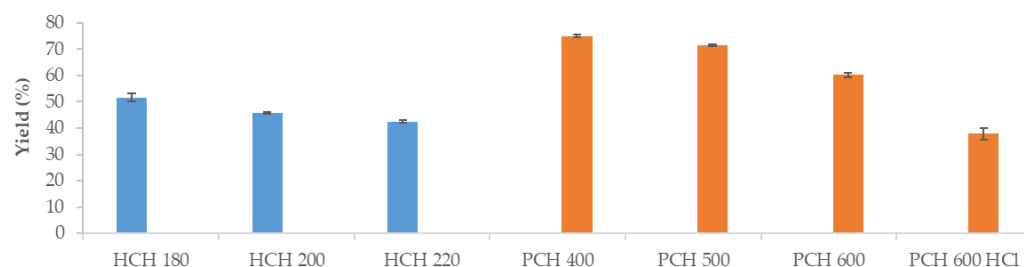


Figure 1. Processing temperature effect on the carbonaceous materials yield. The materials were prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis. The error bars mark the standard deviations ($n = 5$).

A similar decrease in hydrochar yield was reported for *Paulownia* leaves by Koprivica et al. [37], who observed a decline from 41.44% to 24.00% over the 180–260 °C range, and attributed it to hydrolytic conversion of biomass components, deoxygenation, and decarboxylation during HTC. The higher absolute yields obtained in our study may partly reflect differences in feedstock composition and related structural characteristics.

Across all studied conditions, pyrochars consistently gave higher yields than hydrochars [67,68]. HCl treatment of PCH 600 further reduced the yield to 37.88%, indicating the removal of acid-soluble components from the solid matrix [69,70].

The ash content differed substantially between the hydrochar and pyrochar samples (Table 1). The raw biomass contained 6.84% ash, whereas the hydrochars had lower ash content, ranging from 3.73% to 4.97%. In contrast, the pyrochars contained markedly higher ash fractions, increasing from 17.46% at 400 °C to 27.50% at 600 °C. The increase can be assigned to the progressive loss of organic matter due to pyrolysis, which leads to an accumulation of mineral constituents in the residual solid [71–73].

One-way ANOVA revealed that differences in ash content between the studied samples were statistically significant ($p < 0.001$). Tukey’s post hoc test indicated remarkable differences among all sample pairs, confirming that both the conversion route and HCl post-treatment had a pronounced effect on the inorganic fraction of the studied materials.

Unlike pyrochar, where ash enrichment is commonly observed with increasing treatment temperature, ash trends in hydrochar are often more variable and depend heavily on feedstock composition, mineralogy, and hydrothermal process conditions, including the extent of inorganic dissolution and redistribution during treatment [74–77]. This variability should be taken into account when comparing hydrochar data across studies, even when the same type of biomass is used.

Table 1. Ash content of carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis at different processing temperatures. Values are presented as mean and standard deviation (SD, $n = 3$).

Sample	Processing Temperature (°C)	Ash Content Mean (%)	Ash Content SD
Biomass	–	6.84	0.06
HCH 180	180	4.14	0.04
HCH 200	200	4.97	0.05
HCH 220	220	3.73	0.04
PCH 400	400	17.46	0.08
PCH 500	500	18.60	0.08
PCH 600	600	27.50	0.10
PCH 600 HCl	600	9.72	0.05

Koprivica et al. [37] reported a related trend for hydrochar prepared from *Paulownia* leaves, where the ash content rose from 5.17% (180 °C) to 5.56% (200 °C) and further to 6.48% at 220 °C. In the present study, ash content likewise increased between 180 and 200 °C, from 4.14% to 4.97%, but then decreased to 3.73% at 220 °C. Thus, although the initial trend was similar, the results indicate that the ash content response at higher HTC temperature was not identical. The lower ash content observed in our HCH 220 sample may indicate more effective removal of part of the mineral fraction during hydrothermal treatment and subsequent washing, whereas in the study by Koprivica et al. [37], mineral retention or redistribution in the solid product appears to have been more pronounced. Overall, this comparison confirms that ash content in hydrochars is influenced not only by temperature, but also by the specific processing and post-treatment conditions applied to the solid product. A pronounced post-treatment effect was also observed for PCH 600, where HCl washing reduced the ash content from 27.50% to 9.72%, revealing that a considerable mineral portion was removed from the pyrochar matrix [68,78–80].

3.2. Active and Exchangeable pH

To extend the physicochemical characterization of the prepared materials, active and exchangeable pH values were determined. Their variation with the conversion route, processing temperature, and post-treatment is presented in Table 2 and depicted in Figure S1.

Table 2. Active and exchangeable pH of carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis at different processing temperatures. Values are presented as mean $\pm$ SD ($n = 3$).

Sample	Processing Temperature (°C)	Active pH	Exchangeable pH
BIOMASS	25	6.369 $\pm$ 0.002	6.202 $\pm$ 0.003
HCH 180	180	5.521 $\pm$ 0.003	5.352 $\pm$ 0.004
HCH 200	200	5.395 $\pm$ 0.001	5.195 $\pm$ 0.005
HCH 220	220	5.370 $\pm$ 0.002	5.213 $\pm$ 0.016
PCH 400	400	6.612 $\pm$ 0.002	6.322 $\pm$ 0.006
PCH 500	500	6.109 $\pm$ 0.008	4.873 $\pm$ 0.007
PCH 600	600	6.130 $\pm$ 0.007	4.859 $\pm$ 0.004
PCH 600 HCl	600	3.992 $\pm$ 0.021	3.863 $\pm$ 0.013

The pH data revealed differences between the hydrochar and pyrochar samples. Compared with raw biomass, all hydrochars exhibited lower active and exchangeable pH values, indicating a shift toward a more acidic character after hydrothermal carbonization. The pyrochars behaved differently. Their active pH remained near neutral, whereas the exchangeable pH decreased more markedly at higher pyrolysis temperatures. The greatest

change was observed after HCl treatment of PCH 600, where active pH decreased to 3.992 and exchangeable pH to 3.863.

These trends indicate that the pH of the carbonaceous materials was affected by conversion route and subsequent post-treatment [13,68,80,81]. However, pH trends in carbonaceous materials remain feedstock and process-dependent, particularly with respect to mineral composition, ash content, conversion severity, and post-treatment conditions [13,68,82,83]. The significantly lower pH of acid-treated pyrochar, together with the marked reduction in ash content after HCl washing, points to a substantial change in the inorganic fraction and overall surface character of the material [81,82]. Based on the literature available to us, direct pH data for carbonaceous materials specifically prepared from *Paulownia tomentosa* leaves appear to be limited, and active and exchangeable pH values have not been identified. The pH of the adsorption system remained close to neutral throughout the experiments, with variations in no more than ± 0.5 pH units. Since pH_{pzc} was not determined, electrostatic interactions cannot be evaluated quantitatively and are discussed only in relation to the measured pH values and the known acid-base properties of the pesticides.

3.3. Oxidizable Organic Carbon Content (C_{oxi})

To further characterize the organic fraction of the prepared materials, C_{oxi} was evaluated. The values are provided in Table S2 and shown in Figure 2.

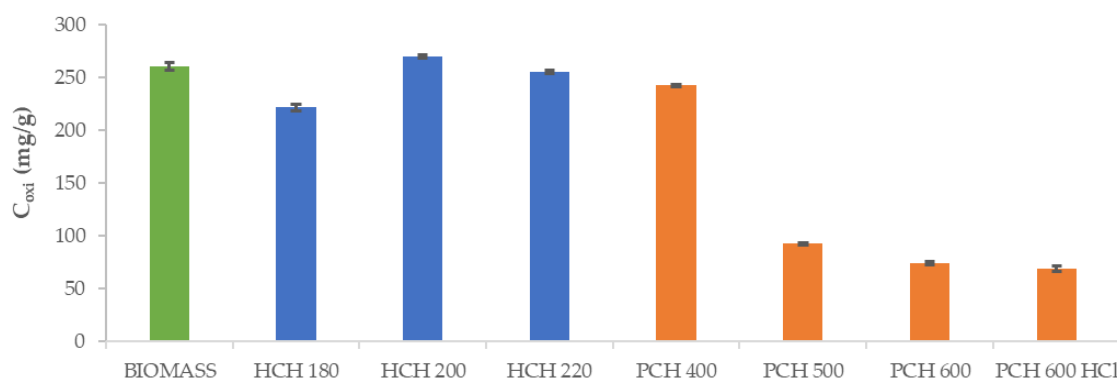


Figure 2. Variation in oxidizable organic carbon content (C_{oxi}) among carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis. Error bars mark standard deviations ($n = 3$).

The C_{oxi} values differed markedly among the analyzed samples. The hydrochars retained relatively high C_{oxi} values, with the highest value recorded for HCH 200. On the contrary, the pyrochars showed a pronounced decline with increasing pyrolysis temperature. Although PCH 400 still exhibited a comparatively high C_{oxi} value, much lower values were observed for PCH 500 and PCH 600, with the lowest value overall observed for the HCl-treated sample.

The relatively high C_{oxi} values observed for the hydrochars and for the PCH 400 sample indicate that a considerable fraction of oxidizable organic structures remained preserved under these conditions. The highest C_{oxi} value was recorded for HCH 200, which may reflect a balance between partial transformation of the biomass and retention of oxidizable organic structures under moderate HTC conditions, rather than simple preservation of the original biomass composition. In contrast, the sharp decrease observed for PCH 500 and PCH 600 points to a much stronger transformation of the organic matrix at higher pyrolysis temperatures, where the material likely became less susceptible to oxidation by dichromate due to progressive carbonization and structural condensation [84–86].

A slight decrease in C_{oxi} was observed after HCl treatment of PCH 600, which may reflect mineral removal and changes in the accessibility of oxidizable organic structures after acid washing [87,88]. However, Tukey's post hoc test did not show any major difference between PCH 600 and PCH 600 HCl, despite statistically significant differences in C_{oxi} among the studied samples, as confirmed by one-way ANOVA ($p < 0.001$). This result indicates that HCl washing mainly affected the inorganic fraction and surface accessibility, rather than the oxidizable carbon content of the highly carbonized pyrochar.

3.4. FTIR Analysis

FTIR analysis was used to monitor changes in surface functional groups during hydrothermal carbonization, slow pyrolysis, and subsequent acid treatment. For clarity, the spectral evolution is discussed stepwise in Figures 3–5, while the combined FTIR spectra for all samples are provided in Figure S2. The spectra were interpreted mainly based on the presence, disappearance, and relative intensity changes in characteristic absorption bands.

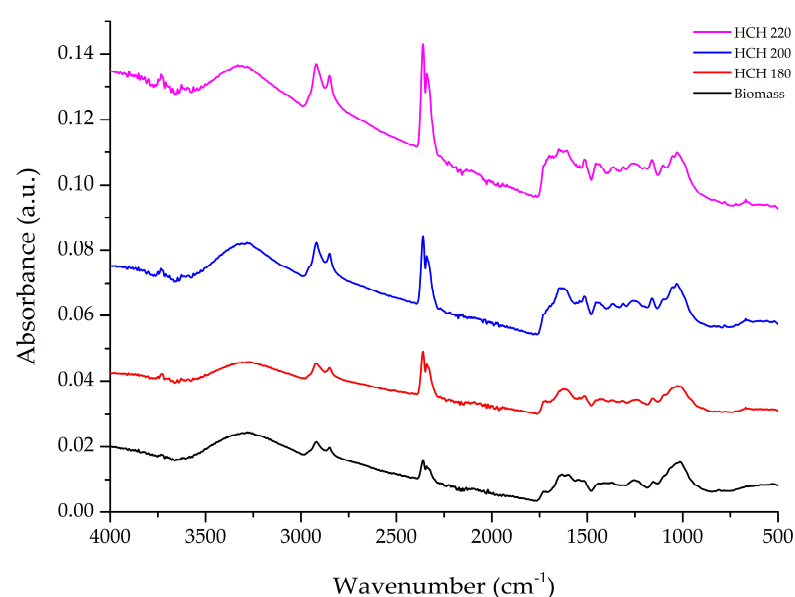


Figure 3. FTIR spectra of biomass and hydrochars prepared from *Paulownia tomentosa* leaves at 180, 200, and 220 °C.

The FTIR spectrum of the raw biomass contained a broad band at 3330–3270 cm^{-1} that can be assigned to O–H stretching vibrations of either adsorbed H_2O or hydroxyl groups. Bands near 2920 and 2850 cm^{-1} can be assigned to aliphatic C–H stretching. The absorption region at 1260–1015 cm^{-1} can be assigned to C–O–C and C–O vibrations of polysaccharide structures. A band near 1635 cm^{-1} corresponds to H–O–H bending vibrations of adsorbed H_2O , with possible contributions from conjugated C=C and C=O groups. A 2350 cm^{-1} band corresponds to atmospheric CO_2 and is not related to the sample composition.

The hydrochar samples retained the main spectral features of the raw biomass, but visible changes in band intensity and resolution already indicated chemical transformation during HTC. The persistence of the C–H and O–H bands suggests an incomplete elimination of hydroxyl and other oxygen-containing functional groups. At the same time, changes in the 1600–1650 cm^{-1} region became more pronounced, particularly for HCH 220, suggesting the gradual development of conjugated structures and the onset of aromatization. The bands in the 1160–1020 cm^{-1} region remained clearly visible throughout the hydrochar series, indicating that C–O-containing groups were still preserved. In this respect, the hydrochars may be regarded as an intermediate stage between the raw biomass and the more strongly transformed pyrochars. This interpretation is in accordance with Ko-

privica et al. [89] for hydrochars prepared from *Paulownia* leaves, where HTC was likewise associated with a decrease in oxygen-rich biomass features and a gradual development of more aromatic structures. Their spectra also showed reduced O–H intensity and increasing aromatic contributions with increasing HTC severity, supporting the trend observed here for HCH 180–HCH 220.

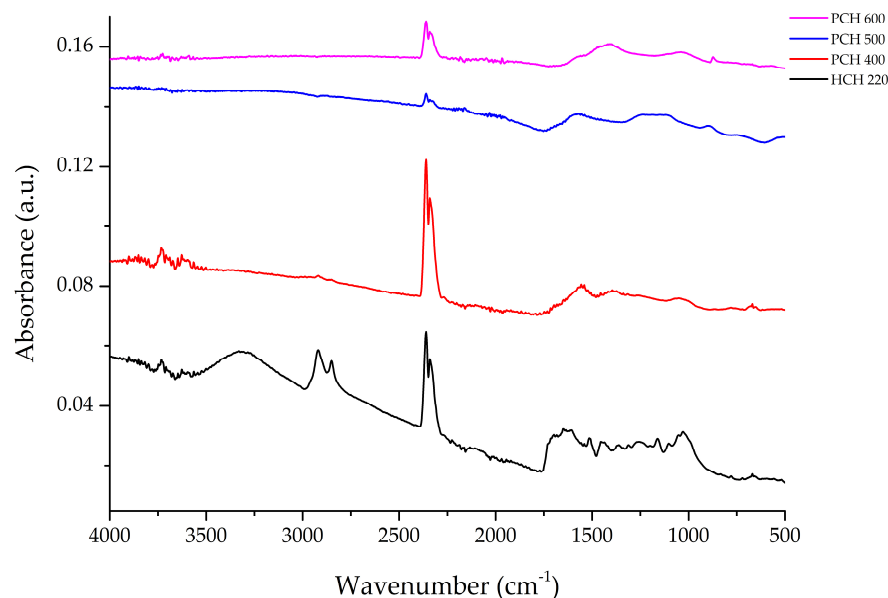


Figure 4. FTIR spectra of HCH 220 and pyrochars prepared from *Paulownia tomentosa* leaves at temperatures of 400, 500, and 600 °C.

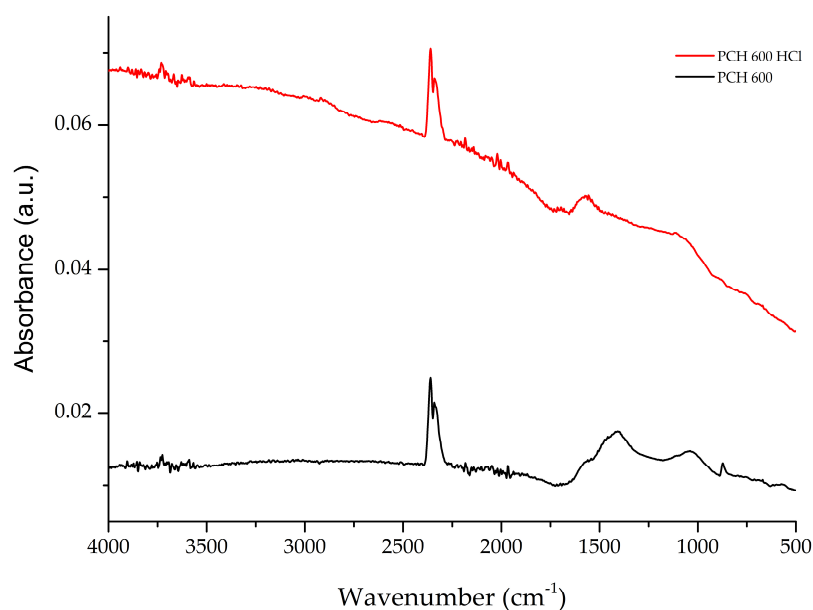


Figure 5. FTIR spectra of PCH 600 and acid-treated pyrochar (PCH 600 HCl) prepared from *Paulownia tomentosa* leaves.

The FTIR spectra of HCH 220 and the corresponding pyrochars show a clear progression in surface chemistry during pyrolysis (Figure 4). Compared with HCH 220, a marked decline in the O–H band intensity at around 3300 cm^{-1} is observed as temperature increases, suggesting progressive dehydration and the removal of hydroxyl-containing functional groups.

The stretching bands of aliphatic C–H bonds ($\sim 2920, 2850 \text{ cm}^{-1}$), still visible in HCH 220, progressively diminish and nearly disappear at higher pyrolysis temperatures, re-

flecting the decomposition of aliphatic structures and the advancement of carbonization. Concurrently, the bands at $1200\text{--}1000\text{ cm}^{-1}$, corresponding to C–O–C and C–O, markedly decrease in intensity, confirming the breakdown of oxygen-containing functionalities derived from polysaccharides.

In contrast, the intensity of the $1600\text{--}1650\text{ cm}^{-1}$ band region becomes more pronounced with increasing temperature, particularly for PCH 500 and PCH 600. This change is related to the increasing fraction of aromatic structures (C=C) and increasing level of structural condensation, in agreement with the formation of a more carbonized and aromatized material.

The FTIR spectra of PCH 600 and PCH 600 HCl (Figure 5) differ mainly in band intensity rather than in band position. The absence of C–H bands and the very weak O–H band around $\sim 3300\text{ cm}^{-1}$ confirm the advanced degree of carbonization, while a weak band at $\sim 1600\text{--}1650\text{ cm}^{-1}$ marks the formation of condensed aromatic structures. The decrease in intensity in the $1500\text{--}1000\text{ cm}^{-1}$ region after HCl washing suggests the removal of ash-related inorganic components rather than major changes in the carbon framework. As noted by Ilić et al. [90], FTIR has limited interpretative value for highly carbonized materials; therefore, the observed spectral changes should be interpreted in conjunction with the results of complementary characterization methods.

Taken together, the spectra show a gradual transformation of the raw biomass into increasingly carbonized materials (Figure S2). The hydrochars retained more biomass-derived features, including C–H, O–H, and C–O–C/C–O bands, whereas pyrochars, especially those prepared at 500 and 600 °C, showed a weaker contribution of these bands and a more pronounced aromatic character. The spectrum of PCH 600 HCl remained close to that of PCH 600, although the fingerprint region appeared less affected by spectral background disturbances.

These spectral changes correspond well to the other physicochemical parameters determined in this study. The preservation of oxygen-containing bands in the hydrochar series agrees with their relatively high C_{oxi} values and lower pH, whereas the gradual weakening of C–O and O–H related bands in the pyrochar series matches the marked decrease in C_{oxi} and the stronger carbonization reached at higher pyrolysis temperatures [4,91].

In the acid-treated sample, the less disturbed spectral background and fingerprint region are consistent with the decrease in ash content and pH after HCl washing, indicating that the treatment mainly affected the inorganic fraction and surface-associated components [4,91–93]. A similar connection between FTIR-visible changes in surface chemistry and altered adsorptive behavior was also noted by Petrović et al. [94] for modified hydrochar systems. Overall, the FTIR results support the gradual transition from oxygen-rich biomass to increasingly condensed carbonaceous materials, with the most pronounced structural changes observed in the high-temperature pyrochars.

3.5. Surface and Pore Properties Determined by CO_2 Adsorption

The surface and pore properties of the prepared carbonaceous materials were evaluated from CO_2 adsorption data acquired at 273 K using DFT analysis. The obtained values are summarized in Table 3. The CO_2 -derived surface area was strongly influenced by the conversion route, processing temperature, and post-treatment. Hydrochars exhibited relatively low surface areas, ranging from 38.0 to $45.2\text{ m}^2/\text{g}$. In contrast, pyrochars showed substantially higher surface areas, especially at higher pyrolysis temperatures. The surface area increased from $134.2 \pm 3.3\text{ m}^2/\text{g}$ for PCH 400 to $321.5 \pm 8.6\text{ m}^2/\text{g}$ for PCH 500. A slightly lower value was observed for PCH 600, namely $297.8 \pm 6.0\text{ m}^2/\text{g}$, while the highest surface area was recorded for the acid-treated pyrochar, PCH 600 HCl, reaching $398.9 \pm 3.1\text{ m}^2/\text{g}$.

Table 3. Surface and pore properties of carbonaceous materials derived from *Paulownia tomentosa* leaves via hydrothermal carbonization and slow pyrolysis at different processing temperatures.

Sample	Processing Temperature (°C)	Surface Area (m ² /g)	CO ₂ -Accessible Pore Volume (cm ³ /g)
HCH 180	180	45.2 ± 2.4	0.015 ± 0.001
HCH 200	200	41.9 ± 1.8	0.013 ± 0.001
HCH 220	220	38.0 ± 0.4	0.012 ± 0.001
PCH 400	400	134.2 ± 3.3	0.042 ± 0.001
PCH 500	500	321.5 ± 8.6	0.082 ± 0.006
PCH 600	600	297.8 ± 6.0	0.077 ± 0.004
PCH 600 HCl	600	398.9 ± 3.1	0.108 ± 0.002

The CO₂-accessible pore volume followed a similar trend. Hydrochars showed low pore volume values between 0.012 and 0.015 cm³/g, whereas pyrochars exhibited higher values, indicating more pronounced development of CO₂-accessible microporosity during pyrolysis. The highest pore volume was observed for PCH 600 HCl, with a value of 0.108 ± 0.002 cm³/g. This increase after HCl treatment can be attributed mainly to the removal of minerals and ash-forming components from the pyrochar matrix, which may have improved the accessibility of narrow pores. All analyzed materials exhibited predominantly micro- and ultramicroporous characteristics, with the dominant pore width below 1 nm. The DFT fitting errors were below 0.75% for all samples, indicating good agreement between the experimental CO₂ adsorption data and the applied DFT model. However, because CO₂ adsorption at 273 K mainly probes narrow micropores and ultramicropores, the obtained pore volume values should be interpreted as CO₂-accessible pore volumes rather than total pore volumes covering the complete micro-, meso-, and macropore range.

The hydrochars exhibited relatively low CO₂-derived surface area values, which decreased slightly with increasing HTC temperature, from HCH 180 to HCH 220. Under the applied hydrothermal conditions, the development of CO₂-accessible microporosity therefore remained limited. At the same time, the hydrochar series retained a substantial fraction of oxygen-containing structures, as reflected in the FTIR results and the relatively high C_{oxi} values. Similar behavior has been reported for hydrochars prepared under moderate HTC conditions, where only limited surface area development is typically observed despite the retention of oxygen-containing surface groups [95,96].

A different trend was observed for the pyrochars. Their CO₂-derived surface area increased strongly from PCH 400 to PCH 500, indicating a more pronounced development of CO₂-accessible microporosity during pyrolysis than during HTC. This trend is consistent with the progressive loss of O-bearing functional groups (as indicated by FTIR spectra) and the pronounced decrease in C_{oxi} at higher pyrolysis temperatures. A similar temperature-dependent increase in surface area has been reported for pyrochars and biochars prepared from various lignocellulosic feedstocks, where higher pyrolysis temperatures promoted devolatilization, pore formation, and the development of a more carbonized structure. At the same time, FTIR analyses in these studies showed a decline in O-bearing functional groups and an enrichment of aromatic bonds, which agrees with the spectral changes and C_{oxi} decline observed in the present study [97–99].

A slight decrease in CO₂-derived surface area was then observed for PCH 600 compared with PCH 500. This indicates that a further increase in pyrolysis temperature did not continue to improve CO₂-accessible surface development to the same extent. This behavior may be related to structural rearrangement of the pore system at higher thermal severity. Similar plateau-like behavior or slight decreases in surface area at the highest pyrolysis temperatures have been observed in other studies and are commonly attributed to pore

widening, partial pore collapse, or reorganization of the carbon matrix under more severe thermal treatment [100–102].

The highest CO₂-derived surface area and CO₂-accessible pore volume were recorded for PCH 600 HCl. Together with the marked decrease in ash content after HCl washing, this indicates that acid treatment removed part of the mineral fraction that may have blocked or partially occupied narrow pores, thereby increasing the accessibility of the porous structure to CO₂ molecules. This interpretation is also consistent with the FTIR results, where the acid-treated sample showed a smoother baseline and a less-disturbed fingerprint region. A comparable increase in surface area after chemical treatment has been described for modified biochars and pyrochars, where acid washing or post-pyrolysis activation removed mineral matter and improved pore accessibility [23,103,104].

Although the increase in CO₂-accessible surface area and pore volume suggests improved textural development of pyrochars compared with hydrochars, adsorption performance cannot be explained solely by surface area. The interaction of metribuzin and tebuconazole with the prepared materials is also affected by surface chemistry, the presence of oxygen-containing functional groups, aromaticity, hydrophobicity, ash content, and the accessibility of adsorption sites in aqueous media. Therefore, the textural parameters should be interpreted together with FTIR results, pH values, C_{oxi} values, ash content, and adsorption data.

3.6. Morphological Analysis

SEM analysis was utilized to investigate morphological changes in the raw biomass and selected carbonaceous materials prepared from *Paulownia tomentosa* leaves. HCH 220 was selected as a representative hydrochar sample because it represents the highest HTC temperature used in this study and thus the most thermally transformed material within the hydrochar series. Representative images at 250× and 1500× magnification are shown in Figures 6 and 7, respectively, while Figure 8 focuses on PCH 600 and PCH 600 HCl.

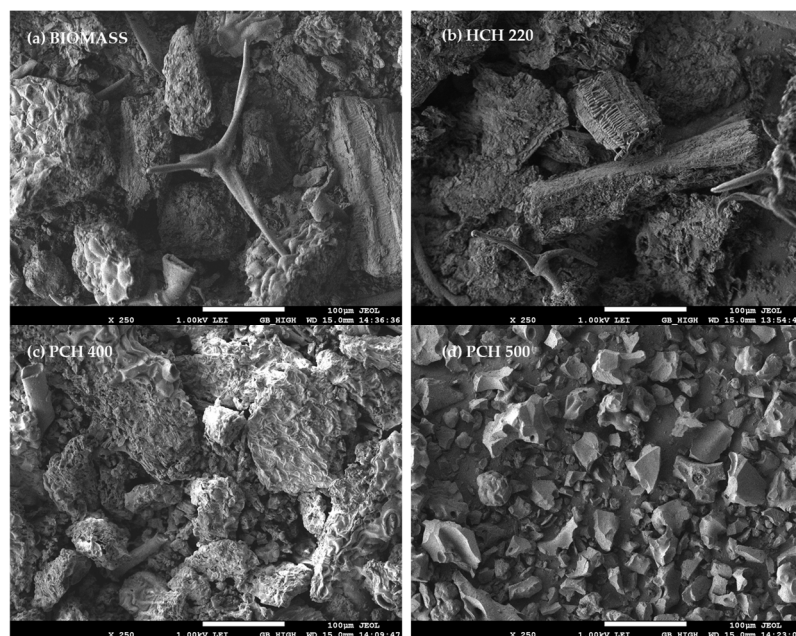


Figure 6. SEM images of dry ground biomass and selected carbonaceous materials prepared from *Paulownia tomentosa* leaves at 250× magnification: (a) raw biomass, (b) HCH 220, (c) PCH 400, and (d) PCH 500.

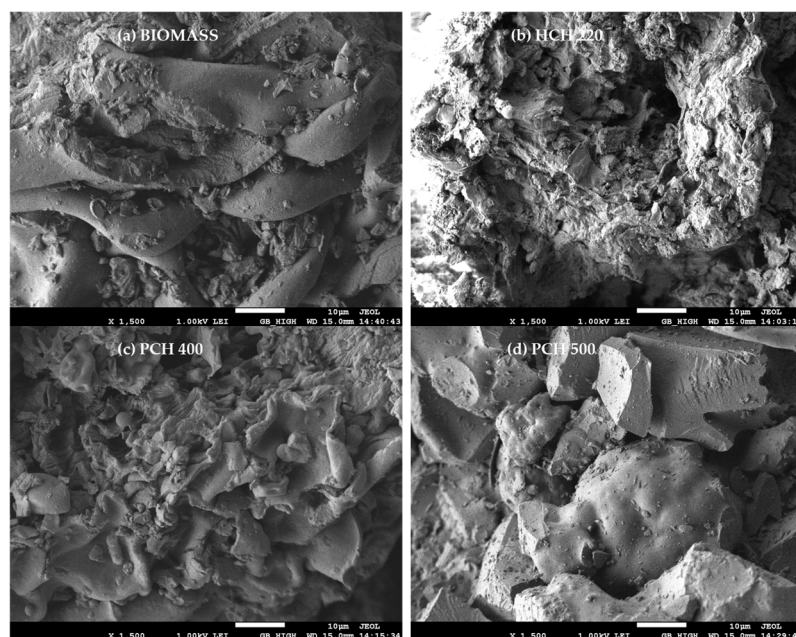


Figure 7. SEM images of dry ground biomass and selected carbonaceous materials prepared from *Paulownia tomentosa* leaves at 1500× magnification: (a) raw biomass, (b) HCH 220, (c) PCH 400, and (d) PCH 500.

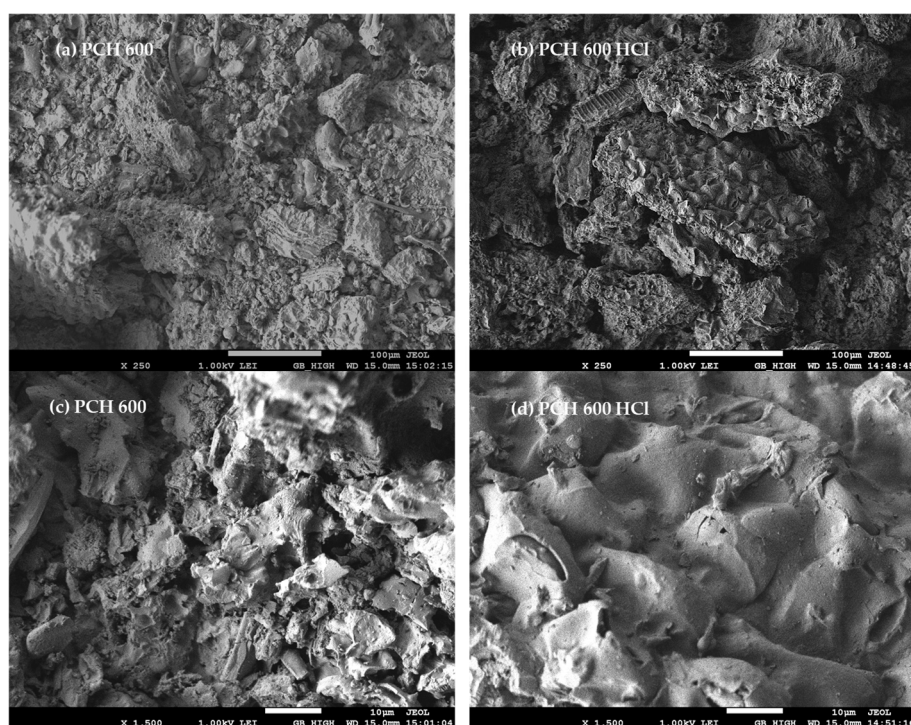


Figure 8. SEM images of PCH 600 and HCl-treated pyrochar PCH 600 HCl prepared from *Paulownia tomentosa* leaves: (a) PCH 600 at 250× magnification, (b) PCH 600 HCl at 250× magnification, (c) PCH 600 at 1500× magnification, and (d) PCH 600 HCl at 1500× magnification.

The raw biomass consisted of irregular fragments of mechanically disrupted leaf tissue with visible fibrous and plant-derived structural features (Figures 6a and 7a). No pronounced thermally induced surface development was observed, and the morphology mainly reflected mechanical grinding. In the HCH 220 sample, several biomass-derived structural features were still recognizable, including fibrous fragments and partially preserved cellular residues (Figures 6b and 7b). At the same time, the surface appeared

locally compacted and disrupted, indicating partial transformation of the original biomass structure under HTC conditions. This agrees with the FTIR and C_{oxi} results, which showed that hydrochar retained a considerable fraction of oxygen-containing and oxidizable organic structures.

More pronounced morphological changes were observed for the pyrochars prepared at 400 and 500 °C (Figure 6c,d and Figure 7c,d). These samples consisted of more fragmented particles with rougher surfaces and visible cavities or openings. The progressive disruption of the original plant tissue can be associated with devolatilization and thermal decomposition of biomass components during pyrolysis. These observations are consistent with an increase in CO_2 -derived specific surface area, particularly for PCH 500, although SEM captures larger-scale surface features and should not be interpreted as direct evidence of microporosity.

The PCH 600 sample showed a heterogeneous and fractured morphology, with strongly disrupted particles and visible voids (Figure 8a,c). After HCl treatment, the PCH 600 HCl sample exhibited a more open and rougher surface, with deeper channels and exposed cavities visible at higher magnification (Figure 8b,d). This observation is in accordance with the marked decline in ash content and increase in specific surface area after acid washing. Therefore, the SEM results suggest that HCl treatment removed part of the mineral fraction and improved surface accessibility, rather than causing a major restructuring of the carbon framework.

A comparable irregular morphology was reported by Koprivica et al. [37] for hydrochar prepared from *Paulownia* leaves at 220 °C, where SEM revealed stacked structures with pores of varying dimensions; chemical modification further produced cracks, folds, holes, and channels, which were associated with improved access to active sites.

Similar morphological changes in pyrochars have been linked to devolatilization and thermal degradation of cellulose, hemicellulose and lignin during pyrolysis, which promote tissue disruption, fracture formation, and surface heterogeneity [14,105,106].

Acid-induced removal of mineral and ash-forming components has also been reported to unblock surface regions and increase surface accessibility [107,108]. In the present study, this interpretation is supported by the lower ash content and higher CO_2 -derived specific surface area of PCH 600 HCl. Since SEM reflects mainly larger-scale morphology, these observations should be interpreted together with CO_2 adsorption/DFT-derived textural parameters, FTIR, C_{oxi} , and ash-content data rather than as direct evidence of microporosity.

3.7. Adsorption Kinetics

The adsorption kinetics of tebuconazole and metribuzin on the studied carbonaceous materials were evaluated using the PFO and PSO models. The calculated kinetic parameters of these models are given in Table 4. For metribuzin, the model with the lower SSE value was considered to provide the better fit. For tebuconazole, the PFO and PSO fits were retained only for numerical comparison because the experimental profiles were non-monotonic and neither model adequately described the complete time-dependent behavior.

For metribuzin, the PSO model provided a more reliable fit for all tested sorbents, as indicated by lower SSE compared to those of the PFO model. The fitted equilibrium adsorbed amount, q_e , generally increased from the hydrochar series to the pyrochar series and reached the highest values for the acid-treated sample, PCH 600 HCl. The adsorption equilibrium was achieved within approximately 8 h for most samples. Representative kinetic curves are shown in Figure 9.

Table 4. Kinetic parameters obtained from nonlinear fitting of the PFO and PSO models for metribuzin (MB) and tebuconazole (TB) adsorption on hydrochars and pyrochars prepared from *Paulownia tomentosa* leaves. For metribuzin, the lower SSE value was used to identify the better-fitting model. For tebuconazole, the reported SSE values provide only a numerical comparison because neither model adequately represented the complete non-monotonic kinetic profiles.

Model	Parameter	HCH 180		HCH 200		HCH 220		PCH 400		PCH 500		PCH 600		PCH 600 HCl	
		MB	TB	MB	TB	MB	TB	MB	TB	MB	TB	MB	TB	MB	TB
PFO	Qe (mg/g)	0.58	4.94	0.71	5.17	0.88	5.50	1.07	3.61	0.87	3.51	1.52	3.99	4.42	5.55
	k ₁ (1/min)	0.16	0.36	0.18	0.33	0.07	0.35	0.00	0.05	0.01	0.04	0.02	0.11	0.07	0.16
	SSE	0.21	1.38	0.29	1.26	0.29	0.99	0.16	5.96	0.16	5.38	0.69	11.65	4.17	5.17
PSO	Qe (mg/g)	0.65	5.01	0.78	5.26	0.95	5.57	1.21	4.02	0.95	3.88	1.64	4.38	4.70	5.84
	k ₂ (g/mg min)	0.17	0.21	0.20	0.16	0.09	0.19	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.04
	SSE	0.16	1.39	0.22	1.28	0.19	1.12	0.11	3.80	0.09	3.44	0.40	9.27	2.11	3.64
Model with lower SSE *		PSO	PFO	PSO	PFO	PSO	PFO	PSO	PSO	PSO	PSO	PSO	PSO	PSO	PSO

* Note: For tebuconazole, the model with the lower SSE is reported only as a numerical comparison. Because the experimental kinetic profiles were non-monotonic, neither the PFO nor the PSO model adequately described the complete adsorption course, and the fitted parameters should not be used for reliable mechanistic interpretation.

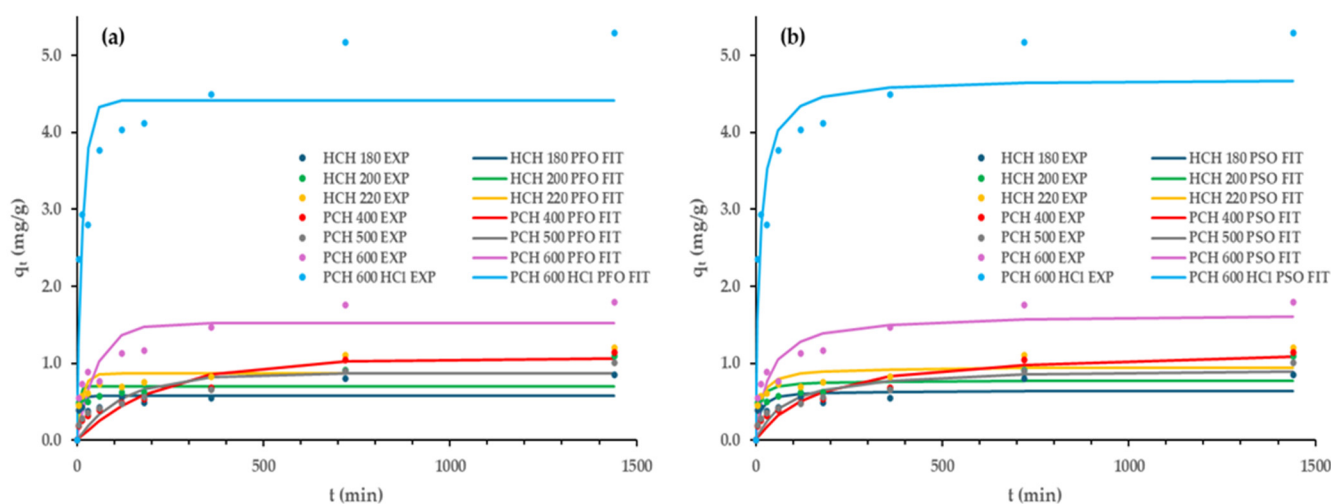


Figure 9. Nonlinear adsorption kinetic curves for metribuzin on carbonaceous materials prepared from *Paulownia tomentosa* leaves: (a) PFO model and (b) PSO model. Symbols represent experimental data points, while lines represent the fitted kinetic models.

The better agreement with the PSO model suggests that metribuzin uptake was strongly influenced by surface-related interaction. However, this should not be interpreted as direct proof of a single chemisorption mechanism, because pseudo-order kinetic models are empirical descriptions and may reflect several simultaneous processes. In the present study, the hydrochars retained more oxygen-containing functional groups, as indicated by FTIR and higher C_{oxi} values, which may have supported hydrogen bonding and other polar interactions with metribuzin. In contrast, pyrochars showed more carbonized surfaces and higher CO_2 -accessible surface and pore properties, which may have improved the accessibility of adsorption sites. Therefore, metribuzin uptake was likely governed by a combination of surface chemistry and textural accessibility rather than by surface area alone.

Similar behavior has been reported for metribuzin adsorption on carbonaceous materials, where the PSO model often provides a better fit and is associated with adsorption controlled by surface-related interactions involving oxygen-containing functional groups [109–111].

In contrast to metribuzin, tebuconazole showed non-monotonic kinetic behavior. For the hydrochar samples, the differences between the PFO and PSO models were small, with slightly lower SSE values for the PFO model. For the pyrochar samples, the PSO model generally produced lower SSE values than the PFO model, although neither model adequately represented the complete non-monotonic kinetic profiles. The highest SSE values were observed for PCH 600, indicating that neither model described this system particularly well. Acid treatment reduced the SSE values for PCH 600 HCl, especially for the PSO model; however, this numerical improvement did not resolve the inability of the models to reproduce the decrease in q_t at longer contact times. Because the experimental q_t values initially increased and subsequently decreased at longer contact times, neither the PFO nor the PSO model adequately described the complete kinetic profile. Therefore, a stable adsorption equilibrium could not be unequivocally identified for tebuconazole, and the fitted parameters should be interpreted only as empirical descriptors. Representative kinetic curves are shown in Figure 10.

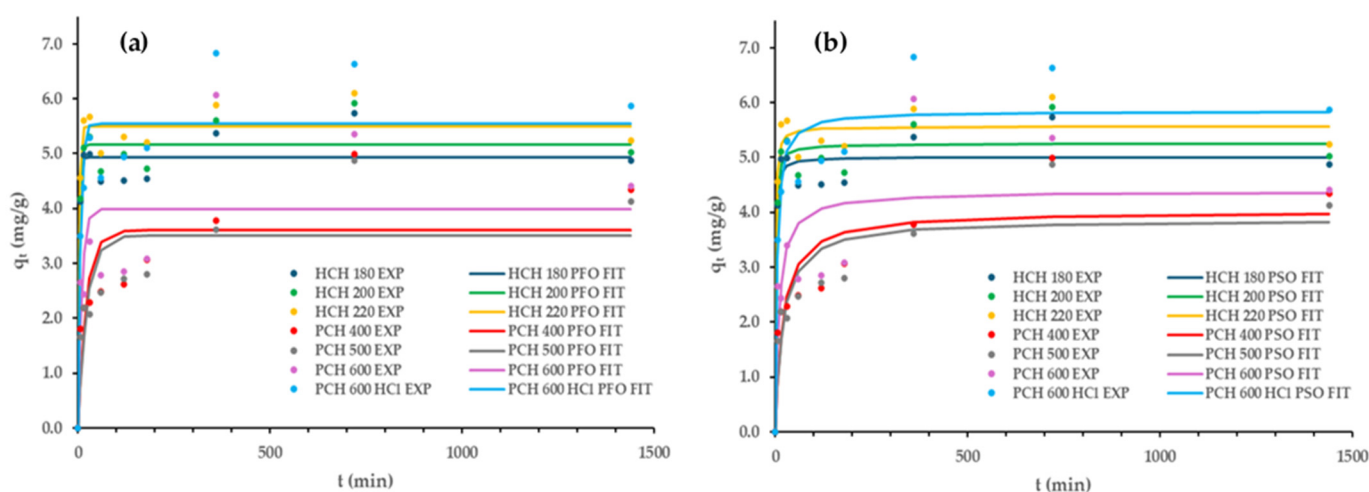


Figure 10. Nonlinear adsorption kinetic curves for tebuconazole on carbonaceous materials prepared from *Paulownia tomentosa* leaves: (a) PFO model and (b) PSO model. Symbols represent experimental data points, while lines represent the fitted kinetic models.

The less regular kinetic behavior of tebuconazole may be associated with its lower aqueous solubility and more hydrophobic character compared with metribuzin. Rapid initial uptake at short contact times resulted in the non-monotonic shape of several kinetic curves. This decrease may indicate partial desorption or redistribution of tebuconazole between the adsorption sites and the aqueous phase after initial uptake. In addition, the heterogeneous surface structure of the prepared carbonaceous materials and the different availability of polar functional groups, aromatic domains, and CO₂-accessible pores may have affected tebuconazole uptake. However, desorption was not directly quantified in the present kinetic experiment; therefore, this interpretation should be regarded as a working hypothesis rather than as a confirmed mechanism. Dedicated adsorption–desorption experiments are currently in progress to evaluate the reversibility of tebuconazole retention, and their results will be reported separately.

For the pyrochar samples, the PSO model generally produced lower SSE values than the PFO model. Nevertheless, the lower SSE values do not demonstrate that the PSO model correctly represents the adsorption mechanism because the model does not reproduce the subsequent decrease in experimental q_t values. A similar numerical preference for the PSO model was reported for tebuconazole adsorption on modified sludge-based biochar [112]. In the present study, however, the non-monotonic profiles indicate that tebuconazole uptake may involve adsorption followed by redistribution or partial release,

which cannot be represented by conventional two-parameter PFO and PSO models. Consequently, no mechanistic conclusions were drawn from the fitted PFO and PSO parameters for tebuconazole.

Previous studies on tebuconazole adsorption by P-doped and ZnCl₂-modified biochars identified pore filling, π - π interactions, hydrogen bonding, hydrophobic interactions, and/or surface complexation as relevant adsorption mechanisms [113,114]. These interactions may also have contributed to the rapid initial uptake observed in the present study. However, because the complete tebuconazole kinetic profiles were not adequately represented by either the PFO or PSO model, the fitted q_e values cannot be reliably interpreted as equilibrium-adsorbed amounts. The higher initial uptake observed for several pyrochars and for PCH 600 HCl may be associated with the increased CO₂-derived surface area, higher CO₂-accessible pore volume, reduced ash content, and improved accessibility of carbonized surface domains. Nevertheless, the subsequent decrease in q_t indicates that the retention of tebuconazole may not have been fully irreversible under the applied conditions.

3.8. Adsorption Isotherm Modeling

The adsorption isotherms of metribuzin and tebuconazole were analyzed using the nonlinear Langmuir model and the Freundlich equation. The calculated isotherm parameters are summarized in Table 5. The suitability of the isotherms differed depending on the pesticide and sorbent type, indicating that the adsorption behavior was affected by both the surface properties of the carbonaceous materials and the physicochemical characteristics of the pesticide.

Table 5. Parameters obtained from nonlinear fitting of the Langmuir model and the Freundlich equation for the adsorption of metribuzin (MB) and tebuconazole (TB) on carbonaceous materials prepared from *Paulownia tomentosa* leaves.

Sorbent	Pesticide	K_F	n	R^2_F	SSE_F	K_L (L/mg)	q_{max} (mg/g)	R^2_L	SSE_L	Better-Fitting Isotherm
HCH 180	MB	0.03	1.00	0.998	0.0096	0.0005	67.76	0.998	0.0104	Freundlich
	TB	1.76	2.05	0.491	9.2870	0.2457	7.31	0.521	8.7470	Langmuir
HCH 200	MB	0.06	1.11	0.989	0.0795	0.0026	17.54	0.990	0.0752	Langmuir
	TB	1.94	1.83	0.254	14.1500	0.2225	9.07	0.271	13.8300	Langmuir
HCH 220	MB	0.04	0.97	0.999	0.0126	0.0002	271.12	0.998	0.0198	Freundlich
	TB	2.51	2.51	0.511	9.5160	0.4807	6.95	0.629	7.2240	Langmuir
PCH 400	MB	0.09	1.26	0.993	0.0495	0.0051	10.33	0.988	0.0857	Freundlich
	TB	2.44	7.21	0.077	16.5270	1.0386	3.84	0.188	14.5350	Langmuir
PCH 500	MB	0.05	1.15	0.949	0.2110	0.0016	20.19	0.945	0.2300	Freundlich
	TB	2.82	10.93	0.078	15.7060	4.1520	3.68	0.213	13.4080	Langmuir
PCH 600	MB	0.51	2.27	0.992	0.0595	0.0514	4.11	0.933	0.4840	Freundlich
	TB	3.10	14.09	0.044	25.7970	5.6200	3.89	0.180	22.1430	Langmuir
PCH 600 HCl	MB	5.29	6.45	0.920	6.5110	0.1128	12.14	0.754	19.9630	Freundlich
	TB	4.55	5.47	0.692	8.5360	13.5888	5.56	0.703	8.2190	Langmuir

Note: K_F is expressed in (mg/g) (L/mg)^{1/n}. SSE is expressed in (mg/g)². The better-fitting isotherm was selected based on a higher R^2 value and lower SSE value.

For metribuzin, the Freundlich equation provided a better fit for most of the studied sorbents, including HCH 180, HCH 220, PCH 400, PCH 500, PCH 600, and PCH 600 HCl, as indicated by higher R^2 values and lower SSE values. Only HCH 200 was slightly better described by the Langmuir model. This result suggests that metribuzin adsorption was generally associated with heterogeneous adsorption sites rather than with ideal monolayer adsorption on energetically uniform surfaces.

In the hydrochar series, the Freundlich constants remained relatively low, indicating limited adsorption affinity toward metribuzin under the studied conditions. Although the Langmuir model yielded a high q_{max} value for HCH 220, this value should be interpreted with caution because the Langmuir constant was very low and the Freundlich equation

provided the better overall fit. Therefore, the Langmuir-derived $q_{\max}$ for this sample should not be considered a direct measure of practically attainable adsorption capacity.

For the pyrochar series, the preference for the Freundlich equation became more evident at higher pyrolysis temperatures. This indicates a more heterogeneous distribution of adsorption sites in the more carbonized samples. The increase in K_F for PCH 600 and especially for PCH 600 HCl suggests improved metribuzin affinity after more severe thermal treatment and subsequent acid washing. The acid-treated pyrochar showed the highest K_F value for metribuzin, which is consistent with its increased CO_2 -derived surface area, higher CO_2 -accessible pore volume, and reduced ash content. These changes likely improved the accessibility of adsorption sites and enhanced interactions between metribuzin and the carbonaceous surface.

For tebuconazole, the Langmuir model provided a slightly better mathematical fit for all studied sorbents based on the combined R^2 and SSE criteria. However, the overall fit quality was weak for several TB datasets, particularly for HCH 180, HCH 200, PCH 400, PCH 500, and PCH 600. Therefore, the Langmuir fit for tebuconazole should be interpreted mainly as an empirical description of the experimental data rather than as strong evidence of ideal monolayer adsorption.

The weaker fit of both isotherm equations for tebuconazole indicates that its equilibrium behavior was less regular than that of metribuzin. This agrees with the kinetic results, where tebuconazole also showed less uniform adsorption behavior. The lower suitability of simple Langmuir and Freundlich descriptions may be related to the low aqueous solubility and higher hydrophobicity of tebuconazole, rapid uptake at lower concentrations, possible redistribution between solution and sorbent surface, and the heterogeneous character of the prepared carbonaceous materials.

Despite the poorer model fits for tebuconazole, the fitted parameters indicate a relatively high affinity toward several prepared materials. This may be related to its more hydrophobic character, which can promote interactions with carbon-rich and aromatic domains. However, because the R^2 values were low for several TB systems, these parameters should be interpreted cautiously and not overused for mechanistic conclusions.

Overall, the isotherm analysis showed that metribuzin adsorption was more consistently described by the Freundlich equation, especially for pyrochars and the acid-washed pyrochar, suggesting the importance of surface heterogeneity. In contrast, tebuconazole was formally better described by the Langmuir model, but the low R^2 values and high SSE values for several systems indicate that its adsorption behavior was more complex and not fully captured by the applied two-parameter isotherm equations.

The preference for the Freundlich equation in several metribuzin systems, particularly for the more carbonized and acid-washed samples, is consistent with previous observations for metribuzin adsorption on high-temperature wood-derived biochar. In that study, Freundlich-type fitting was attributed to adsorption on heterogeneous carbonaceous surfaces. However, the cited work used poplar wood gasification biochar prepared at 850 °C; therefore, the comparison should be understood mechanistically rather than as a direct capacity comparison [115].

For tebuconazole, Yang et al. [112] reported adsorption onto modified sludge-based biochar, with a Langmuir-derived maximum capacity of 7.865 mg/g, and emphasized the influence of pH, textural properties, and FTIR-detectable surface groups on adsorption behavior. Higher capacities reported for P-doped corn straw biochar were associated with a much larger surface area, the presence of functional groups, and Langmuir-type adsorption. The proposed mechanisms included hydrogen bonding, pore filling, π - π interactions, and hydrophobic interactions [113].

These comparisons support the interpretation that the isotherm behavior observed in the present study was governed by both surface heterogeneity and pesticide-specific interactions. However, absolute adsorption capacities should not be directly compared, because the cited studies used different feedstocks, conversion routes, chemical modifications, and experimental conditions.

4. Conclusions

This study evaluated carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization, slow pyrolysis, and HCl post-treatment. The conversion route and processing temperature strongly affected yield, ash content, pH, oxidizable organic carbon content, surface functionality, morphology, and CO₂-derived surface and pore properties. Hydrochars retained more oxygen-containing and oxidizable organic structures, whereas pyrochars showed stronger carbonization, higher ash content, higher CO₂-derived surface area, and more fragmented morphology.

HCl treatment of PCH 600 reduced ash content and increased CO₂-accessible surface and pore properties, indicating improved surface accessibility. SEM and FTIR results suggest that acid washing mainly affected mineral and surface-associated components, without substantial restructuring of the carbon framework. This is also supported by C_{oxi} results, which showed no statistically significant difference between PCH 600 and PCH 600 HCl.

Adsorption behavior differed between the pesticides. Metribuzin adsorption was better described by the PSO kinetic model for all sorbents and was most strongly enhanced after HCl treatment of PCH 600. Tebuconazole showed generally higher initial uptake on the prepared materials, but its kinetic behavior was non-monotonic, with a decrease in the adsorbed amount at longer contact times for several sorbents. Therefore, neither the PFO nor the PSO model adequately described the complete kinetic profiles, and their fitted parameters were not used for mechanistic interpretation. The observed decrease may indicate partial desorption or redistribution, although this hypothesis requires confirmation by dedicated adsorption–desorption experiments. Nonlinear isotherm modeling showed that metribuzin adsorption was predominantly described by the Freundlich equation, suggesting heterogeneous adsorption sites, whereas tebuconazole was formally better described by the Langmuir model, although with poorer fit quality for several materials.

The results support the working hypothesis that changes in the conversion route, processing temperature, and post-treatment modify the materials' physicochemical properties and influence pesticide-specific adsorption behavior. Overall, *Paulownia tomentosa* leaves are a suitable precursor for carbonaceous sorbents, with HCl-treated PCH 600 showing the most promising performance for metribuzin adsorption. However, its lower material yield after acid washing should be considered in future scale-up and publication studies. Control experiments confirmed pesticide stability, negligible handling losses, stable pH conditions, and no relevant HPLC-UV interference from sorbent-derived leachates at the monitored wavelengths. However, long-term sorbent stability, detailed leaching behavior, regeneration potential, and performance in real water matrices should be evaluated in future application-oriented studies. In addition, dedicated adsorption–desorption experiments are currently being conducted to verify whether the decrease in tebuconazole uptake at longer contact times results from reversible desorption or redistribution between the sorbent and aqueous phases.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/technologies14070396/s1>. Table S1: Yield values of carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis at different processing temperatures. Table S2. Oxidizable organic carbon content (C_{oxi}) of

carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis at different processing temperatures. Values are given as mean $\pm$ standard deviation ($n = 3$). Figure S1. Active and exchangeable pH of carbonaceous materials prepared from *Paulownia tomentosa* leaves by hydrothermal carbonization and slow pyrolysis. The error bars are used to mark standard deviations ($n = 3$). Figure S2. Combined FTIR spectra of biomass, hydrochars, pyrochars, and HCl-treated pyrochar prepared from *Paulownia tomentosa* leaves.

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