

Article

Sustainable Textile-Bound Biochar Composites with Peroxidase-like Activity for Dye Decolorization: Proof-of-Concept Study

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Abstract

Efficient adsorbents and nanozyme-like materials are of growing importance in environmental technologies. Here, we report a simple and potentially scalable approach for the immobilization of biochars onto nonwoven acrylic textiles, yielding composite materials with good retention of immobilized biochar during aqueous treatment and combined adsorption and peroxidase-like activities. The structure of native and biochar-modified textiles was characterized by scanning electron microscopy and small-angle X-ray scattering, confirming the presence of biochar particles on fiber surfaces and within the inter-fiber space, as well as nanoscale structural changes induced by biochar incorporation. Textile-bound biochars exhibited peroxidase-like activity toward *N,N*-diethyl-*p*-phenylenediamine in the presence of hydrogen peroxide and enabled effective decolorization of methylene blue. Adsorption alone resulted in 61% dye removal after 240 min, while the combined adsorption-catalytic process achieved 74% decolorization. Modification of the textile-bound biochar with copper ions further enhanced the peroxidase-like activity, increasing dye removal to 85% under identical conditions. The optional incorporation of a magnetic iron wire allows facile magnetic handling of the composite. Owing to its low cost, simplicity of preparation, and dual functionality, the textile-bound biochar composite represents a promising proof-of-concept platform that may warrant further development for dye removal and related environmental applications.



Academic Editor: Rajesh Mishra

Received: 9 May 2026

Revised: 8 July 2026

Accepted: 9 July 2026

Published: 14 July 2026

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Keywords: biochar; nonwoven textile; peroxidase-like activity; dye decolorization

1. Introduction

Biochar is a carbon-rich material produced from a wide range of biological materials (biomass) or biological waste through pyrolysis in the absence of oxygen in various reactor types. Biochar has several important properties, including high carbon content, large surface area, stable structure, cation exchange capacity, nutrient retention, and pollutant removal, and at the same time, biochar is a low-cost material [1,2]. Biochar is intensively studied currently in different directions, including improving crop yield, water purification, alternative fuels, air purification, catalysis, biogas production, purification, and storage [1].

An especially important application of low-cost, high-efficiency biochar adsorbents is the removal of a wide variety of environmental pollutants, thus substituting for more expensive activated carbon [3,4]. The rapidly growing number of publications indexed in Web of Science further illustrates the increasing scientific interest in biochar-based sorbents and environmental applications. Emerging contaminants (a group of relatively low-concentration but high-toxicity pollutants in the environment, including, e.g., antibiotics, endocrine-disrupting chemicals, polychlorinated biphenyls, caffeine, drugs, etc.) have been successfully removed using both native and modified biochars [3]. Also, a wide variety of other organic contaminants, including pesticides, polycyclic aromatic hydrocarbons, dyes, etc., have been removed using biochars prepared from different precursors under various pyrolysis conditions [5]. Biochars have also been successfully used to treat water contaminated with heavy metals due to their superior ability to adsorb heavy metal ions [4,6]. Designed biochars with enhanced functionality have been involved in the efficient removal of radioactive cesium and strontium from water [7]. Biochars also have great potential for treating industrial wastewater containing various contaminants, including phenolic compounds, heavy metal ions, oils, pesticides, pharmaceuticals, and other industrial by-products [8].

Biochars have been widely investigated for the removal of organic dyes from contaminated water owing to their low cost, tunable surface chemistry, and adsorption capacity [9–13]. Among various model dyes, methylene blue (MB) is frequently employed because of its well-defined spectroscopic properties, stability, and widespread use in adsorption [14] and catalytic decolorization studies. While numerous studies have focused on powdered biochar sorbents, considerably less attention has been paid to biochar immobilized on textile substrates, particularly in systems combining adsorption and peroxidase-like catalytic activity.

Numerous studies have investigated the adsorption of methylene blue on biochars prepared from different feedstocks and under various pyrolysis conditions [15–24]. The adsorption behavior is commonly described using Langmuir and/or Freundlich isotherm models, while adsorption kinetics are frequently fitted by pseudo-second-order models [15–18]. Reported adsorption capacities range from several tens to several hundreds of mg/g, depending on the biochar precursor, preparation conditions, and experimental setup [15–24]. In addition to native biochars, chemically modified and magnetically responsive biochars have also been developed to improve adsorption performance and facilitate material recovery [23,24]. Collectively, these studies indicate that the adsorption of methylene blue by biochar has already been extensively characterized, whereas considerably less attention has been devoted to exploiting the intrinsic peroxidase-like activity of biochars for simultaneous adsorption and catalytic dye removal.

In 2020, biochars were first reported to exhibit peroxidase-like (P-L) activity, as demonstrated by the catalytic oxidation of chromogenic substrates such as *N,N*-diethyl-*p*-phenylenediamine (DPD) and 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of hydrogen peroxide [25]. This finding opened new possibilities for the use of biochar not only as an adsorbent but also as a catalytic material for pollutant degradation. The biochar P-L activity is influenced by several factors, including the type of biological material used for the preparation of biochar, the pyrolysis temperature and time, the size of the resulting biochar particles, and any potential modification of the biochar formed. The biochar P-L activity enabled the decolorization of crystal violet, both in model solutions and in pond water containing various impurities. Previous studies suggest that biochar can activate hydrogen peroxide and generate reactive oxidizing intermediates, including hydroxyl radicals, which may contribute to pollutant degradation [25]. In addition, algae-derived biochar exhibiting P-L activity has been employed for the construction of nanozyme arrays for the discrimination and detection of multiple pesticides in soil, water, and food. High-performance biochar nanozyme sensor arrays could discriminate pesticides in a concentration range from 1 to 500 μM and in real samples from soil, lake water, seawater, apples, cucumbers, peaches, tomatoes, and cabbage. Furthermore, pesticides could be quantified down to 1 μM [26].

Despite these promising findings, the immobilization of peroxidase-like biochars on practical macroscopic supports and the combined exploitation of their adsorption and catalytic properties have received only limited attention. Therefore, the present study explores the application of biochar peroxidase-like activity for methylene blue decolorization.

Immobilization of both adsorbents and catalysts on insoluble carriers has improved their reusability in various environments [27,28]. Especially important are magnetic carriers, which can be selectively separated from the solutions and suspensions using appropriate magnetic separators [29].

Textile materials represent low-cost carriers that exhibit important advantages such as high surface area, flexibility, and mechanical strength [30]. Textile materials have been efficiently used for immobilization of enzymes [31,32], polysaccharides [33,34], ionic liquids [35], affinity ligands [36], or (nano)particles [37–40]. A recent review chapter summarized the magnetic nanofinishes for textiles in detail [41]. Current development of the textile industry leads to the high production of various types of textiles and textile waste. The reuse of waste textiles is thus of high importance, and their application as a low-cost carrier and subsequent conversion into an efficient adsorbent/catalyst is of interest [42].

This work aligns with the European Union's circular economy action plan, which promotes sustainable product life cycles through waste prevention, resource efficiency, and the prolonged use of materials with maximized value extraction. In this study, we report a simple approach for the immobilization of different biochars onto native and magnetically modified nonwoven textiles. The binding of biochar particles and the structural characteristics of the resulting composites at both micro- and nanoscales were investigated using scanning electron microscopy and small-angle X-ray scattering (SAXS). The resulting textile–biochar composites exhibited dual functionality, combining adsorption capacity with peroxidase-like activity, and enabled effective decolorization of selected organic dyes. To the best of our knowledge, the combined immobilization of biochar on nonwoven textiles with simultaneous exploitation of its adsorption capacity and intrinsic peroxidase-like activity for dye decolorization has not been previously reported.

2. Materials and Methods

2.1. Materials

White 100% acrylic nonwoven textile (Bastelfilz, 10 cm × 30 cm) was from Max Bringmann KG-folia, Wendelstein, Germany. Hydrogen peroxide (30%), copper(II) sulfate pentahydrate, and other common chemicals were from Lach-Ner, Neratovice, Czech Republic. *N,N*-Diethyl-*p*-phenylenediamine sulfate salt (DPD), Congo red (Direct Red 28; Color Index Number 22120), methylene blue (Basic Blue 9; Color Index Number 52015), and Bismarck brown Y (Basic Brown 1; Color Index Number 21000) were from Sigma-Aldrich, Prague, Czech Republic. NdFeB magnetic testing rod (diameter 30 mm) and small permanent magnets (20 × 10 mm) were from Magsy, Fryšták, Czech Republic. An office stapler and common iron-based staples were obtained locally. Biochar-4073 (BCH-4073), produced by Biouhel.cz (Zlín, Czech Republic), was prepared by pyrolysis of soft wood at 750 °C for 40 min. Biochars provided by co-author M.J.Y. were prepared from hemp biomass supplemented with potato pulp, both in the raw form (BCH-HHPP550) and in pellet form (BCH-HHPP550P), by pyrolysis at 550 °C for ca. 30 min in an auger reactor. The nonwoven textile and biochars used in this study were selected due to their low cost, availability, and compatibility with scalable and sustainable processing routes.

2.2. Modification of Nonwoven Textile with Biochar

The biochars used in this study were first ground using a knife laboratory mixer (Microtron Kinematika 550, Kinematica GmbH, Eschbach, Germany). The ground biochars were sieved through a 100 µm sieve. The biochar fraction below 100 µm was selected to facilitate adhesion to textile fibers and promote uniform surface coverage. In all cases, several batches of biochar-modified nonwoven textiles were prepared. In the case of BCH-4073, 20 pieces of nonwoven textile (2 × 2 cm) were immersed in the biochar suspension (500 mg of biochar in 100 mL of methanol) at room temperature for 4 h under mixing on a horizontal shaker. Modified textile samples were dried in a hood at laboratory temperature. For BCH-HHPP550 and BCH-HHPP550P, this procedure was repeated once more due to the less efficient binding of biochars to the textile. The majority of the textile squares with bound biochar were modified by pressing in a dedicated device (Thermo Press provided by Rea, Šicí Technika Brother s.r.o., Prostějov, Czech Republic) at 200 °C for 90 s and then washed with distilled H₂O and air-dried again. Thermal pressing was applied to improve the fixation of biochar particles within the textile structure, thereby enhancing mechanical stability and reducing particle loss during subsequent aqueous experiments. Biochar loading was determined gravimetrically from the difference in dry mass before and after modification.

Biochar release from thermally modified samples was determined gravimetrically after incubation of individual biochar-modified textile samples in 200 mL of water on a standard horizontal shaker at room temperature for 24 h; then the textile sample was removed, dried, and the mass was measured. All experiments were performed in duplicate.

Part of the BCH-4073-modified textile squares was immersed in 200 mL of a 5% (*w/v*) CuSO₄·5H₂O solution overnight at room temperature under mixing, then washed with water and dried.

2.3. Determination of Peroxidase-like Activity

The peroxidase-like activity of biochar-modified textile materials was determined similarly to that described previously [37]. The assay was performed in a reaction mixture containing 3.4 mL of deionized water (pH 7.0), 400 µL of DPD solution (12.53 mmol/L), and 200 µL of 2% H₂O₂. The reaction was initiated by the addition of one-half of a biochar-modified textile square (1 × 2 cm Figure 1) in the reaction mixture. The samples were

incubated under mixing at room temperature (22 °C) for 10 min. The absorbance at a wavelength (λ) of 551 nm was measured [43] using a Cintra 20 spectrophotometer (GBC Scientific Equipment, Braeside, Australia), and then the absorbance of the corresponding blank reaction mixture lacking the biochar-modified textile was subtracted from all measurements. All measurements were performed in triplicate, and arithmetic means and standard deviations were calculated [37]. Peroxidase-like activity was expressed per unit textile area to reflect the performance of the immobilized composite under practical application conditions.

2.4. Adsorption and Decolorization of Organic Dyes

For adsorption and decolorization experiments, each thermally treated biochar-modified textile square (2 × 2 cm) was cut into two halves (1 × 2 cm) originating from the same textile sample. One half was used to evaluate dye removal by adsorption alone in the absence of hydrogen peroxide, whereas the other half was used to assess dye removal resulting from the combined action of adsorption and peroxidase-like catalysis in the presence of hydrogen peroxide. This approach minimized variations in biochar loading between the samples compared. Experiments were carried out in test tubes containing 4.83 mL of the aqueous dye solution at the specified concentration. To distinguish between the two removal pathways, either 170 μ L of deionized water or 30% H₂O₂ was added to the corresponding tubes. Thermally treated textile squares without bound biochar were used as negative controls. All experiments were conducted at 20 °C for 240 min under identical conditions. Dye removal was monitored by spectrophotometric measurement of solution absorbance at defined time intervals (5–30 min). After each absorbance measurement, the reaction solution and textile sample were returned to the original reaction vessel to maintain identical experimental conditions throughout the experiment. Absorbance was monitored at the characteristic wavelength (λ) of each dye, as specified in the Results. All experiments were performed at least in duplicate, and representative curves are shown. Adsorption isotherms and formal kinetic modeling were not performed in this proof-of-concept study; the experiments were designed to compare relative dye removal under adsorption-only and combined adsorption–catalytic conditions.

2.5. Small-Angle X-Ray Scattering

SAXS measurements were performed at the BioSAXS beamline P12 (EMBL/DESY, Hamburg, Germany) [44]. Two-dimensional SAXS patterns were recorded using a PILATUS 6M pixel detector (DECTRIS AG, Baden-Daettwil, Switzerland) [45] at an X-ray energy of 10 keV and a sample–detector distance of 3 m, covering a momentum transfer range of $q = 0.02$ – 5.5 nm^{-1} ($q = 4\pi/\lambda \sin \theta$, where 2θ is the scattering angle).

SAXS data were collected for nonwoven textiles modified with biochar BCH-4073 and for unmodified nonwoven textile samples used as references; in both cases, measurements were performed on native and thermally treated textiles. To assess sample homogeneity, scattering patterns were recorded from several different positions on each specimen. Azimuthal averaging of the recorded two-dimensional scattering patterns—after masking intermodule gaps of the detector as well as shadows from the beam stop and flight tube—was carried out using the SASFLOW pipeline [46]. The resulting one-dimensional SAXS profiles were scaled to account for differences in sample thickness, compared for consistency, and averaged. Scattering contributions from air and instrumental background, measured in the absence of a sample, were subsequently subtracted. All SAXS data were analyzed and fitted using the SASView software package (version 5.05).

2.6. Electron Microscopy

The surface morphology and microstructural features of thermally treated native nonwoven textile fibers and textiles modified with biochar BCH-4073 were examined using

scanning electron microscopy (SEM). SEM observations were performed with a JEOL JSM-7900F scanning electron microscope (JEOL Ltd., Akishima, Japan) operated at accelerating voltages of 1.0 or 1.5 kV. The analysis focused on evaluating fiber morphology, surface coverage, and the distribution of biochar particles on and between the textile fibers.

3. Results and Discussion

3.1. Deposition of Biochar on Nonwoven Textile

Nonwoven textiles represent attractive carriers for the immobilization of particulate materials due to their high surface area, porosity, and mechanical flexibility. However, the effectiveness of nonwoven textiles as carriers strongly depends on the methods used for particle incorporation and on the mechanical and chemical stability of the immobilized particles within the textile structure, which directly affect their performance during practical applications [31,47].

A simple methanol-based modification procedure was employed to prepare nonwoven textile squares loaded with different types of biochar (Figure 1), and several batches of each material were produced. Methanol improved wetting of both the hydrophobic biochar surface and the nonwoven textile fibers, reduced surface tension, and facilitated penetration of the suspension into the porous textile structure. In addition, its high volatility also enabled rapid solvent evaporation after impregnation, leaving the biochar particles deposited on/within the textile matrix without introducing non-volatile residues. The extent of biochar binding depended on both the biochar type and the specific batch of nonwoven textile used. For biochar BCH-4073, a single modification step resulted in loadings ranging from 4.5 to 14.4 mg per textile square (2×2 cm). In contrast, biochars BCH-HHPP550 and BCH-HHPP550P required a second modification cycle to achieve sufficient deposition, yielding loadings of 10.2 and 11.2 mg per square, respectively. The achieved loadings demonstrate that substantial amounts of biochar can be immobilized on the textile substrate using a simple impregnation procedure.

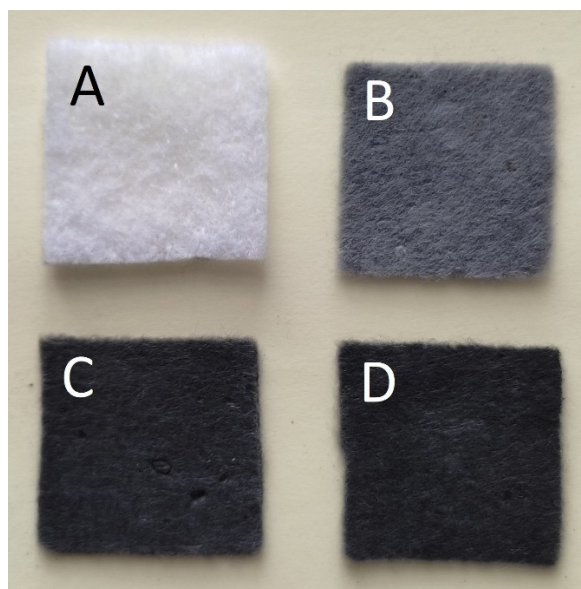


Figure 1. Representative appearance of thermally treated nonwoven textile squares modified with different amounts of biochar BCH-4073. Native textile (A) and textiles loaded with 4.5 mg (B), 7.1 mg (C), and 14.4 mg (D) of biochar per 4 cm^2 textile square. Increasing biochar loading resulted in progressively darker coloration and more extensive surface coverage of the textile.

Thermal pressing markedly improved particle fixation and reduced biochar loss during aqueous storage or dye decolorization experiments. Experimentally, it was found that

2–3% of biochar was released from the above-mentioned thermally pressed textile-biochar samples during 24 h incubation in water. When required, magnetically responsive textile composites can be readily prepared by incorporating a small piece of iron wire (staple) into the textile matrix using an office stapler, thus enabling facile magnetic separation from reaction mixtures, as demonstrated previously [37].

The combination of substantial biochar loading, good retention of biochar particles after thermal treatment, and optional magnetic handling suggests that the developed composites may be of interest for aqueous treatment applications requiring simple operation and low-cost materials, although this remains to be validated beyond the present proof-of-concept stage. In addition, immobilization of biochar on a textile support facilitates handling and recovery of the material compared with powdered biochar systems.

3.2. Characterization of Biochar/Nonwoven Textile Composite

For detailed structural characterization, thermally treated native nonwoven textiles and textiles modified with biochar BCH-4073 (7.1 mg biochar per 4 cm² textile square) were examined. Scanning electron microscopy images of the native and modified textile samples confirmed the presence of biochar particles bound to the surfaces of the textile fibers (Figure 2). The synthetic fibers exhibited diameters of approximately 10 µm, while the majority of biochar particles were in the micrometer size range. In addition to surface-bound particles, a substantial fraction of biochar was observed within the inter-fiber spaces, which contributes to the overall biochar loading and may provide additional accessible surface area for interactions with aqueous pollutants.

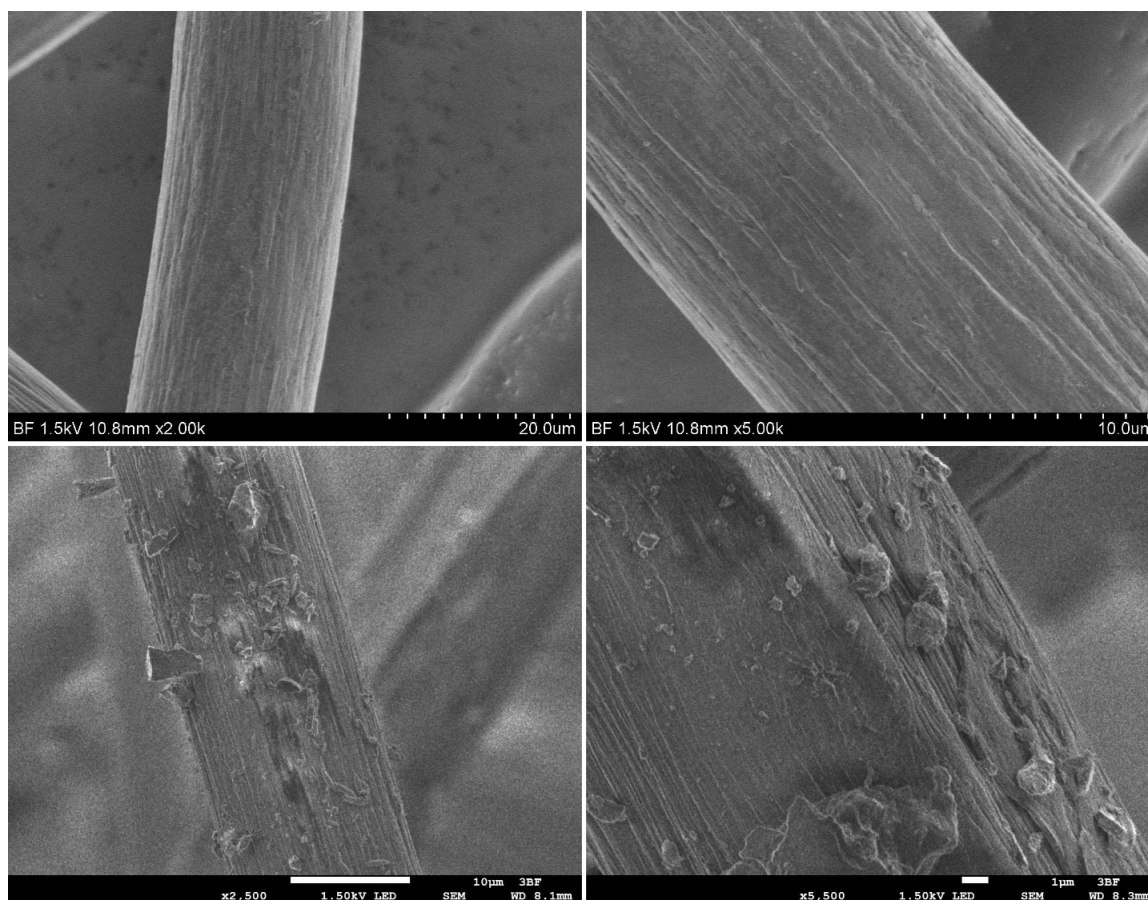


Figure 2. SEM images of thermally treated native nonwoven fibers (**top**) and BCH-4073-modified fibers (**bottom**). Biochar particles are visible on the fiber surfaces and within the porous textile structure. Scale bars: 20 and 10 µm (**top**) and 10 and 1 µm (**bottom**).

The SEM images further suggest that biochar particles are loosely deposited and partially embedded and anchored to the fiber surfaces, which contributes to the mechanical stability of the composite. The increased surface roughness and heterogeneous coverage introduced by biochar immobilization are expected to enhance contact between the composite and aqueous pollutants, thereby supporting both adsorption and catalytic interactions. Importantly, no significant damage or deformation of the textile fibers was observed after thermal treatment, indicating that the modification procedure preserves the structural integrity of the carrier.

3.3. Structural Characterization at the Nanoscale

Small-angle X-ray scattering measurements were performed to characterize the nanoscale structure of the biochar/nonwoven textile composites. The scattering profiles can be divided into two characteristic regions: a low- q region corresponding to larger structural features and a high- q region associated with smaller, nanoscale heterogeneities. The parameters obtained from fitting the experimental SAXS data (Figure 3) are summarized in Table 1.

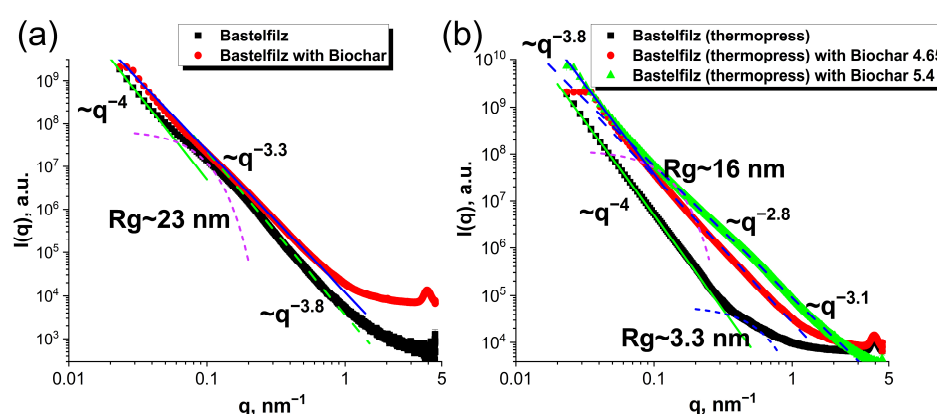


Figure 3. SAXS data for Bastelfilz textile and Bastelfilz textile with bound biochar BCH-4073 particles (a): no thermal treatment; 4.5 mg per textile square (2×2 cm), and for Bastelfilz textile and Bastelfilz textile with bound biochar BCH-4073 particles (b): thermally treated samples. Solid lines are fitted with Guinier and power-law models.

Table 1. Structural parameters derived from SAXS data (Figure 3).

Textile Sample	Low q Region, Power Law Exponent (p)	Large q Region	
		Rg, nm	p
Bastelfilz (no thermal treatment)	4	23	3.8
Bastelfilz with BCH-4073 (no thermal treatment), 4.5 mg per textile square (2×2 cm)	3.3	-	-
Bastelfilz (thermally treated)	4	3.3	-
Bastelfilz with BCH-4073 (thermally treated), 4.65 mg per textile square (2×2 cm)	3.8	-	3.1
Bastelfilz with BCH-4073 (thermally treated), 5.4 mg per textile square (2×2 cm)	3.8	16	2.8

Figure 3a illustrates the effect of biochar immobilization on the native nonwoven textile, highlighting the transition from Porod-type scattering of the pristine fibers to surface-fractal behavior upon biochar addition. In contrast, Figure 3b demonstrates that thermal pressing preserves the overall fiber-scale structure while modifying the nanoscale

organization of the composite, as reflected by changes in the high- q scattering region and reduced radii of gyration. These observations suggest that thermal treatment enhances the structural consolidation of biochar within the textile matrix without compromising the macroscopic integrity of the carrier.

In the low- q region, the scattering intensity of all studied Bastelfilz samples follows a power-law dependence with an exponent close to -4 (Figure 3), which is characteristic of Porod-type scattering from large objects with relatively sharp interfaces and is consistent with the fiber-scale morphology observed by SEM. Upon incorporation of biochar, the low- q power-law exponent decreases to values between -3.3 and -3.8 , indicating a transition toward surface-fractal behavior and a rougher interface. Exponents in the range $3 < |p| < 4$ are commonly associated with increased surface roughness, and the observed changes can be attributed to the presence and attachment of biochar particles on the textile fibers.

In the high- q region, additional scattering contributions are observed for selected samples, with power-law exponents ranging from -2 to -3.1 , suggesting the presence of multilevel or mass-fractal-like nanoscale structures. The corresponding radii of gyration, on the order of approximately 20 nm, indicate the presence of nanoscale structural heterogeneities within the biochar-textile composite. These data complement the SEM observations by revealing a hierarchical structural organization that is not accessible by electron microscopy alone.

It should be mentioned that, although there is almost no effect of biochar addition on the morphology at sizes >100 nm, we see structural reorganization for smaller sizes. Addition of biochar leads to increasing surface roughness (change in power law exponent, fractality of the particles) and surface area (appearance of structural units with small size). Although these morphology changes are not direct proofs of the increase in the surface area, and in the absence of nitrogen sorption data we do not have quantitative information of that, it is plausible to assume that the addition of submicron sized biochar particles increases the surface area accessible to the solution per unit textile area, and this can be a reason for the increase in the composites' efficiency for pollutants adsorption and peroxidase-like activity.

3.4. Peroxidase-like Activity of Studied Biochars

Different types of biochar have been shown to exhibit peroxidase-like activity [25]. Immobilization of enzyme-mimetic particles on nonwoven textiles enables their straightforward handling and application in aqueous systems. The textile-bound biochars investigated in this study exhibited a typical peroxidase-like response upon interaction with a standard peroxidase substrate, *N,N*-Diethyl-*p*-phenylenediamine (DPD), in the presence of hydrogen peroxide. During the reaction, colorless DPD was oxidized to a colored product with a characteristic absorption maximum at 551 nm [43].

The measured peroxidase-like activity depended on both the amount and type of biochar immobilized on the textile. Figure 4 summarizes the average activities expressed per unit textile area (cm^2) to facilitate comparison of immobilized composites, calculated from absorbance changes at 551 nm obtained from three independent measurements and converted to catalytic activity in nanokatal, reflecting the performance of the immobilized composites under application-relevant conditions. The specific biochar P-L activity was 2.41 ± 0.25 nkat/mg for BCH-4073.

As shown in Figure 4, the peroxidase-like activity of the textile-bound biochars strongly depends on both the type and the amount of immobilized biochar. For biochar BCH-4073, the activity increases systematically with increasing biochar loading, indicating that the catalytic response scales with the available amount of active material on the textile surface. Increasing the BCH-4073 loading from 4.5 to 14.4 mg per 4 cm^2 resulted in an approximately

3.6-fold enhancement of peroxidase-like activity, and the observed trend is approximately linear within the investigated range.

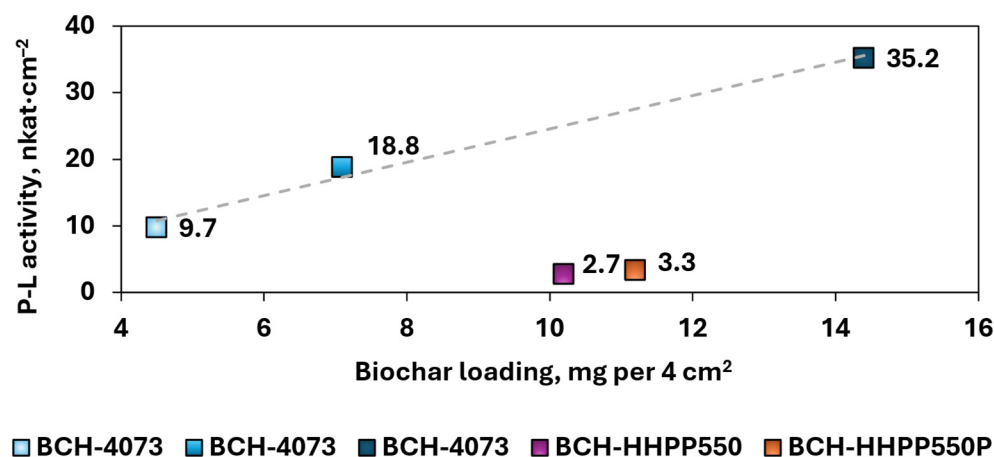


Figure 4. Peroxidase-like activity of thermally treated textile-bound biochars determined using DPD oxidation in the presence of H₂O₂ (max. SD $\pm$ 1.3).

In contrast, biochars derived from hemp with potato pulp (BCH-HHPP550 and BCH-HHPP550P) exhibit substantially lower peroxidase-like activity under identical conditions, despite comparable biochar loadings. These results suggest that the biochar precursor and production conditions, rather than biochar loading alone, influence the enzyme-mimetic performance of the textile-bound composites, an effect that is also reflected in the subsequent dye decolorization experiments. It should be emphasized, however, that the biochars used in this study were not subjected to detailed physicochemical characterization. In the absence of BET surface area, porosity, surface chemistry, pH_{PZC}, elemental/mineral composition, FTIR, Raman, or XPS data, the specific factors responsible for the observed differences in peroxidase-like activity cannot be identified, and these differences should therefore be regarded as phenomenological rather than assigned to any particular intrinsic biochar property.

3.5. Adsorption and Peroxidase-like Properties of Textile-Bound Biochar

Synthetic dyes used in various industrial sectors represent significant environmental pollutants due to their extensive discharge into aquatic systems. In particular, textile dyes often exhibit limited binding to fabrics and are released into wastewater streams, where insufficient treatment can lead to adverse effects on ecosystems and human health. Many organic dyes are toxic to aquatic organisms and may accumulate along the food chain [48].

Recent studies have demonstrated that water-soluble organic dyes and selected aromatic compounds, such as phenols, biphenols, and anilines, can be decolorized through the action of natural peroxidase enzymes (EC 1.11.1.x). Both native and immobilized peroxidases have therefore been explored for dye removal applications [49,50]. However, enzyme-based approaches are often limited by enzyme inhibition in complex water matrices and by the relatively high cost of enzyme production, which restricts their practical and large-scale application in industrial wastewater treatment [51].

Numerous nanozymes exhibiting peroxidase-like activity have been described and evaluated for a wide range of applications [52]. Many of these materials can be produced at relatively low cost and in large quantities, enabling their use as substitutes for natural peroxidase enzymes in environmental remediation. Such nanozyme systems have been explored for the transformation of various toxic and hazardous organic pollutants. In addition to well-known iron oxide nano- and microparticles with peroxidase-like activ-

ity [37,53], several types of biochar have also been shown to exhibit intrinsic peroxidase-like behavior [25,26].

In this study, biochar BCH-4073 immobilized on nonwoven textile (thermally treated, biochar loading of 14.4 mg per 2×2 cm) was investigated for the decolorization of methylene blue (MB), combining adsorption with peroxidase-mimetic activity. MB is a widely used model dye and a persistent organic contaminant that poses risks to environmental and human health when released into aquatic systems. Consequently, the development of environmentally benign and effective approaches for MB removal from water remains an important challenge [54].

Based on these considerations, methylene blue (MB) is widely used as a model dye for investigating adsorption- and enzyme-based decolorization processes. As shown in Figure 5, effective MB removal by adsorption alone was observed for textile-bound biochar BCH-4073 in the absence of hydrogen peroxide, resulting in $60.9 \pm 1.6\%$ dye removal after 240 min. The addition of hydrogen peroxide to the MB solution in the presence of textile-bound biochar led to enhanced decolorization, reaching $74.2 \pm 1.5\%$ removal after 240 min, which can be attributed to the combined contribution of adsorption and peroxidase-like catalytic activity. In contrast, the presence of hydrogen peroxide alone had no measurable effect on MB decolorization under the same conditions. It should be noted that dye removal was quantified spectrophotometrically from the decrease in the characteristic absorbance of methylene blue. These measurements therefore demonstrate decolorization of the dye, but do not by themselves confirm molecular degradation or mineralization of methylene blue, which would require complementary analyses (e.g., LC-MS, TOC/COD measurements, or identification of degradation intermediates).

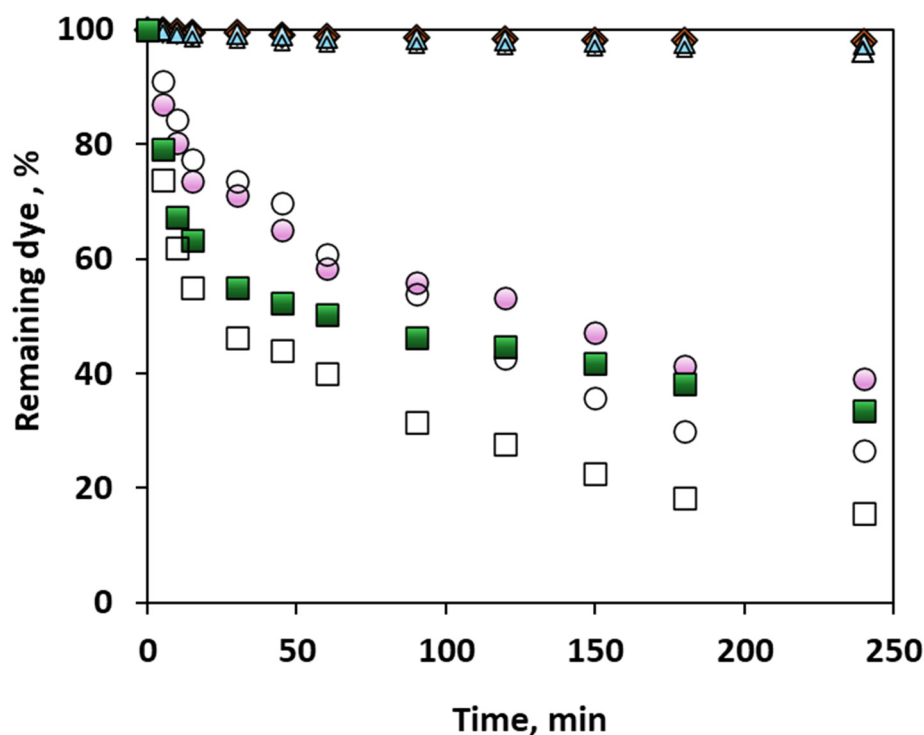


Figure 5. Representative decolorization of methylene blue. (red ♦) MB + H₂O; (pink ♦) MB + H₂O₂; (blue ▲) BF + MB + H₂O; (blue ▲) BF + MB + H₂O₂; (pink ●) BF + BCH-4073 + H₂O; (pink ●) BF + BCH-4073 + H₂O₂; (green ■) BF + BCH-4073 + Cu²⁺ + H₂O; (green ■) BF + BCH-4073 + Cu²⁺ + H₂O₂. The original methylene blue concentration was 100 mg/L.

Textile-bound biochar BCH-4073 also exhibited decolorization activity in fish pond water containing suspended solids and dissolved organic matter (pH 7.3, COD-Cr 52.5 mg/L).

Under these conditions, slightly higher MB removal was observed compared to distilled water. This effect may be attributed to additional adsorption processes and/or biological activity present in the natural water matrix, although a detailed analysis of these contributions was beyond the scope of this study. These preliminary observations in a natural water matrix are intended only to illustrate feasibility and would require systematic evaluation before any conclusions regarding real wastewater performance can be drawn.

Recent studies have demonstrated that selected copper-containing materials, including copper silicate [55] and copper–chitosan composites [56], exhibit pronounced peroxidase-like activity. In addition, copper ions can be efficiently immobilized on biochars derived from various plant-based precursors [57,58]. Based on these observations, textile-bound biochar BCH-4073 was modified with copper ions and subsequently evaluated in decolorization experiments.

Copper-modified biochar exhibited only a marginal improvement in methylene blue adsorption in the absence of hydrogen peroxide, reaching $66.3 \pm 1.4\%$ dye removal after 240 min, compared to the native biochar with $60.9 \pm 1.6\%$ dye removal. In contrast, a substantial enhancement in decolorization efficiency was observed in the presence of hydrogen peroxide, where combined adsorption and peroxidase-like catalysis resulted in $84.9 \pm 1.2\%$ MB removal after 240 min. These results indicate that copper modification primarily enhances the catalytic contribution rather than the adsorption capacity of the textile-bound biochar. Cu-modified biochar is proposed to activate H_2O_2 and exhibit peroxidase-like activity involving ROS-assisted and surface redox pathways. It must be emphasized, however, that this interpretation remains tentative, as the copper-related properties of the composite were not experimentally characterized in the present study. Due to the fact that free copper ions also exhibit P-L and decolorization activities in the presence of hydrogen peroxide, the potential release of copper ions from Cu-biochar and their effect on MB decolorization have to be studied in the future.

The present performance evaluation is intended as a proof-of-concept demonstration rather than a complete adsorption/catalytic study: it is based on time-dependent removal percentages and does not include adsorption isotherms, kinetic modeling, equilibrium adsorption capacities, or a mass balance separating adsorption from oxidative transformation. The comparison with and without hydrogen peroxide therefore gives only a qualitative indication of the catalytic contribution.

Previous studies have shown that biochars can activate hydrogen peroxide to generate reactive intermediates, such as hydroxyl radicals, which can participate in the oxidative transformation of organic dyes, including methylene blue [59]. The partial suppression of DPD oxidation in the presence of isopropyl alcohol, a commonly used hydroxyl radical scavenger, suggests that $\bullet OH$ or related short-lived oxidizing intermediates contribute to the reaction. However, the incomplete inhibition can indicate that DPD oxidation is not governed exclusively by freely diffusing hydroxyl radicals, and that there is a possibility that surface-mediated electron transfer and/or other redox-active intermediates may also participate. The efficiency of this process depends strongly on the properties of the biochar, which are governed by the biomass precursor and the production conditions. As a result, different biochars may exhibit varying affinities toward nonwoven textiles, distinct adsorption capacities for specific pollutants, and different levels of peroxidase-like activity.

In addition to BCH-4073, biochars prepared from hemp with the addition of potato pulp (BCH-HHPP550 and BCH-HHPP550P) were immobilized on nonwoven textiles and evaluated for the decolorization of three organic dyes: Congo red, methylene blue, and Bismarck brown Y. Among the tested dyes, the highest removal efficiencies were observed for Bismarck brown Y, as summarized in Table 2. However, the overall contribution of peroxidase-like activity to dye decolorization was less pronounced for these biochars than

for BCH-4073, consistent with their substantially lower measured peroxidase-like activities (Figure 4). The specific biochar P-L activities were 0.26 ± 0.20 nkat/mg for BCH-HHPP550 and 0.29 ± 0.20 for BCH-HHPP550P.

Table 2. Decolorization of Bismarck brown Y (100 mg/L) using biochars BCH-HHPP550 and BCH-HHPP550P bound to nonwoven textile, both without and with the addition of H_2O_2 .

Biochar Type	Biochar Amount per 2 × 2 cm Textile Square [mg]	Adsorption Without H_2O_2 (240 Min) [%]	Adsorption and Enzyme-like Decolorization with H_2O_2 (240 Min) [%]
BCH-HHPP550	10.2	37.0 ± 0.71	44.5 ± 0.64
BCH-HHPP550P	11.2	43.5 ± 0.91	46.9 ± 1.20

Owing to the simplicity of the preparation procedure and the low cost of both the nonwoven textile and biochar, the developed textile-based adsorbent/catalyst is not primarily intended for regeneration and repeated reuse. Previous studies have shown that regeneration of dye-loaded biochars using water or methanol often results in limited removal of adsorbed dyes [60]. Consequently, appropriate handling and management of exhausted low-cost adsorbents and catalysts after the decolorization process remain important considerations [61]. One potential approach is the repyrolysis of the spent textile-biochar composite to produce regenerated biochar, as both biochar regeneration and the conversion of textile waste into biochar have been demonstrated in recent studies [60,62]. The regenerated biochar can subsequently be applied as an effective adsorbent for a broad range of organic and inorganic pollutants [60,63].

As summarized in Table 3, a wide range of peroxidase-like catalytic systems has been reported for methylene blue decolorization, including metal oxide nanozymes, Prussian blue-based materials, and various biochar-derived catalysts. Many of these systems exhibit high removal efficiencies; however, their application often relies on complex synthesis procedures, nanoparticle recovery steps, or specific operational conditions such as controlled pH or light irradiation. In comparison, the textile-bound biochar developed in this study achieves promising decolorization efficiency under mild conditions at this proof-of-concept stage, while offering practical advantages related to material handling, macroscopic form, and ease of separation from treated water. The integration of adsorption and catalytic activity within a single textile-supported composite represents a distinct design strategy that prioritizes simplicity, scalability, and applicability over maximization of catalytic activity alone.

Table 3. Examples of peroxidase-mimetic materials used for methylene blue decolorization.

Peroxidase-Mimetic Materials	Preparation	Characterization	MB Concentration [mg/L]	pH	Temperature [°C]	Decolorization Efficiency
Biochar-modified textile—this study	Nonwoven textile modified with biochar	Biochar particles are both adsorbed on the surface of textile fibers and trapped in the interfibre space	100	NA	20	Ca 74% MB removal after 240 min with native biochar; 85% MB removal after $CuSO_4$ treatment
Prussian blue NPs (PBNPs) [64]	Co-precipitation technique	PBNPs have a cubic shape and size in the range of 30 to 40 nm.	50	5–7	RT	Degradation of MB within 50 min
Akaganéite (β -FeOOH) [65]	Interaction of $FeCl_3$ with gallic acid or grape seed tannins and urea	Spindle-like shape nanoparticles	10	7	NA	More than 95% MB decolorization within 150 min under green LED light irradiation
$W_{18}O_{49}$ nanospheres [66]	$W(C_2H_5O)_6$ in alcohol was autoclaved for 24 h	100 nm in diameter	20	5	45	Complete degradation of MB was finished in 60 min

Table 3. Cont.

Peroxidase-Mimetic Materials	Preparation	Characterization	MB Concentration [mg/L]	pH	Temperature [°C]	Decolorization Efficiency
Hematite [67]	Transformation of 2-line ferrihydrite NPs	High crystallinity, average size ca. 100 nm	10	8	RT	Complete degradation of MB within 180 min
Porous Co ₃ O ₄ nanorods—reduced graphene oxide [68]	Hydrothermal treatment of cobalt acetate and graphene oxide	Diameters of the individual nanorods were 10–50 nm; their length was 100–500 nm, with a relatively smooth surface	50	6	NA	97% degradation of MB after 25 min
Prussian-blue-modified iron oxide magnetic nanoparticles [69]	Interactions between negatively charged [Fe(CN) ₆] ^{4−} and positively charged γ -Fe ₂ O ₃ NPs	Sphere-like shape of the particles with an average diameter of about 11 nm	300	5.5	25	Complete degradation of MB after 120 min
Copper–chitosan-modified magnetic textile [56]	Nonwoven textile treated with chitosan and CuSO ₄	Cu–chitosan modification of individual fibers and film formation among the fibers	50	NA	22	After 5 h of treatment, 87.5% of MB was removed

NA—not available; RT—room temperature; NPs—nanoparticles. The values reported for the present study refer to dye decolorization determined spectrophotometrically (absorbance decrease); the term “degradation” used for the literature-derived entries reflects the terminology of the corresponding original reports, in which degradation was claimed or experimentally demonstrated.

It should be noted that the studies summarized in Table 3 were performed under different experimental conditions, including variations in dye concentration, pH, catalyst dosage, reaction time, temperature, and the presence or absence of light irradiation. Therefore, the reported removal efficiencies are not directly comparable on a quantitative basis. The purpose of this comparison is to provide a contextual overview of representative peroxidase-like catalytic systems used for methylene blue decolorization and to position the performance of the textile-bound biochar within the broader landscape of reported materials. Nevertheless, the comparison provides a qualitative overview of representative peroxidase-like catalytic systems applied for methylene blue decolorization and highlights key trends in material design and application strategies. In this context, the textile-bound biochar developed in the present study is distinguished by its simple preparation, use of low-cost and readily available materials, absence of complex synthesis steps, and straightforward handling. Unlike many reported nanozyme systems, the proposed composite integrates adsorption and catalytic functionality within a macroscopic, easily recoverable textile support, which is advantageous for potential practical implementation in water treatment applications. Accordingly, this comparison is strictly qualitative and is not intended to rank the catalytic performance of the listed materials; the differences in dye concentration, pH, catalyst dosage, temperature, irradiation conditions, and the nature of the reported outcome (decolorization versus degradation) preclude any direct quantitative ranking.

4. Conclusions

In summary, a simple and low-cost approach was developed for the preparation of textile-bound biochar composites exhibiting combined adsorption and peroxidase-like activity. The structure of the resulting materials was partially characterized using scanning electron microscopy and small-angle X-ray scattering, confirming effective biochar immobilization on the nonwoven textile at both micro- and nanoscales. The immobilized biochar retained its adsorption capacity and enzyme-mimetic activity, and the combined action of these processes in the presence of hydrogen peroxide enabled effective decolorization of methylene blue, reaching up to 85% removal within 4 h under the applied conditions.

The optional incorporation of a magnetic element further simplifies handling by enabling separation of the composite from the treated medium.

As a proof-of-concept, these results indicate that the composite is potentially useful for aqueous dye removal and compatible with simple preparation and handling. Broader implications, including scalability, alignment with circular-economy principles, and end-of-life valorization through repyrolysis into secondary biochar, are presented here as perspectives rather than demonstrated outcomes. Establishing the practical value of the material for sustainable water-treatment applications will require further studies that were beyond the scope of this work, including reusability and long-term stability testing, evaluation of Cu leaching and toxicity for the copper-modified composite, and validation at the process level.

Author Contributions: Conceptualization, I.Š.; Methodology, I.Š., V.P., L.A. and M.J.Y.; Investigation, I.Š., J.P., V.P., L.A., V.M.G., A.J., O.V.K., K.Z.P., L.A.B., P.K. and M.J.Y.; Writing—original draft, I.Š., J.P. and M.J.Y.; writing—review and editing, I.Š., M.J.Y., V.P. and L.A.; Funding acquisition, P.K. and M.J.Y.; Project administration, P.K. and M.J.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the project No. APVV-22-0060 MAMOTEX (Slovak Research and Development Agency, Ministry of Education, Science, Research and Sport of the Slovak Republic), the ERDF project No. CZ.02.1.01/0.0/0.0/17_048/0007399 (Ministry of Education, Youth and Sports of the Czech Republic), project no. 2023/50/O/ST3/00062 (PRELUDIUM BIS) of the Polish National Science Centre, project no. CZ.02.01.01/00/24_037/0013751 (OP JAK-KaMos, NAVRATY_008), project no. WZ/WM-IIM/3/2023 (Polish Ministry of Science and Higher Education) and REA.A—Marie Skłodowska-Curie Actions & Support to Experts within the project 101182948—RETROTRAFO—HORIZON-MSCA-2023-SE-01.

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Acknowledgments: The authors thank Jan Kana (Biouhel.cz) for providing the biochar 4073 sample, Ondrej Masek (UK Biochar Research Centre) for providing the equipment needed to prepare the hemp biochar samples, and Clement Blanchet (EMBL) for his support during SAXS experiments. This work was carried out in the frame of the COST Action CA22134—Sustainable Network for agrofood loss and waste prevention, management, quantification and valorisation (FoodWaStop) and COST Action CA24110—Resource-Inclusive Renewable Materials: Leveraging Global Biomass for Sustainable Innovations (ReInvent).

Conflicts of Interest: All authors declare that there are no competing interests.

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