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Evaluation of Aging Methods on the Surface Characteristics of Hydrochar and Germination Indices for Kale Seeds

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Abstract: Hydrochar derived from hydrothermal carbonization (HTC) has been recognized as a potential absorbent and horticultural substrate. However, its practical application has been limited due to its low adsorption capacity and negative effects on plant growth. To address these issues, three pre-treatment methods (water washing, microbial aging, and freezing-thawing aging) were employed to further improve the physical structure and chemical properties of hydrochar. A seed germination test with kale (*Brassica oleracea* var. *acephala* D.C) was conducted to evaluate the phytotoxicity of modified hydrochars. The results showed that microbial aging considerably enhanced the physicochemical properties of the hydrochar. Specifically, under microbial aging, the bulk density of microbial-aged hydrochar (MHC) decreased by 8.1%, the porosity increased by 24.8%, and the water-holding capacity increased by 36.54% compared to fresh hydrochar (FHC). Moreover, the surfaces of MHC and freezing-thawing aged hydrochar (FTHC) were observed with rough and cracked surfaces and macro pore structures. Fourier transform infrared (FTIR) spectroscopy revealed that the functional group's intensities of the four hydrochar materials varied, and that MHC and FTHC had more oxygen-containing groups than the others. Additionally, the surface areas of MHC and FTHC increased by 318.64% and 238.98% compared to FHC, respectively. The seed germination test indicated the strong inhibitory effect of FHC, while MHC significantly ($p < 0.05$) improved the seed germination rate and root development. These findings suggest that among the different pre-treatment methods, microbial aging demonstrated the greatest potential for practical application in improving the physicochemical properties of hydrochar and promoting seed germination. This study opens up new avenues for further research on improving hydrochar and suggests that future studies should focus on optimizing the aging process.

Keywords: waste treatment; hydrochar; hydrothermal carbonization; soil amendment

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1. Introduction

Horticultural crops are essential for human life and wellbeing, providing vital nutrients and playing a crucial role in maintaining a healthy diet and preventing malnutrition [1,2]. Among them, kale (*Brassica oleracea* var. *acephala* D.C) is a widely cultivated and consumed horticultural product worldwide, and it is also known as a functional food. Kale can be grown and used in various forms, including microgreens (which are edible seedlings), baby greens (young plants), or mature plants. The productivity and quality of kale can be influenced by a variety of factors, such as the quality of the growing medium and environmental stressors. For example, peat is considered a fundamental component of horticultural substrates, but its resources are

limited [3]. Currently, hydrochar has gained more attention as a potential soil amendment and horticultural substrate.

Hydrochar is an emerging solid material created from hydrothermal carbonization (HTC) that can be used for a broad range of applications, including agricultural soil amendment, carbon sequestration, and carbon absorption [4]. As a thermochemical process, HTC is carried out under high temperature and pressure conditions to convert the biomass into a coal-like product (hydrochar) which is characterized by its carbon-rich content and porous structure [5].

Currently, the majority of research has been conducted and proven that biochar is a promising absorbent and soil amendment [6–8]. Compared to pyrolysis biochar, HTC has been shown to offer multiple advantages, such as allowing for the use of wet and dry biomass as feedstocks due to the presence of water as a reaction medium, which means the biomass does not need to be pre-dried [9]. Meanwhile, as the HTC has lower emissions and requires less energy, it creates less pollution with a higher hydrochar yield [10]. However, hydrochar has poor sorption characteristics compared to biochar, such as small surface area and pore volume, which stem from its production process conditions [11]. These characteristics also limit the utilization of hydrochar as an adsorbent, although previous studies have found that hydrochar possesses a range of sorption abilities and can be used as a low-cost adsorbent in certain areas [12–16]. For example, rare-earth ions can be efficiently removed from wastewater by hydrochar produced from kitchen waste [12].

Besides its absorption values, hydrochar is considered a potential soil amendment due to its nutrient-holding capacity and the ability to improve soil physicochemical properties, such as water-holding capacity, water-stable aggregation, pH, and cation exchange capacity [17,18]. These characteristics of hydrochar mainly depend on porosity and surface chemical properties [19]. For instance, nutrients in soils can be adsorbed onto the surface pores of hydrochar and thereby reducing nutrients lost from soil through leaching [18]. Notwithstanding, the presence of toxic compounds in hydrochars, such as phenolic compounds and dioxins, pose some potential risks for inhibiting plant growth and decreasing productivity [20]. However, previous reports have shown that it is necessary to pre-treat hydrochar to reduce its phytotoxicity and render it suitable for use in agricultural soil [21]. From the above, it can be concluded that hydrochar has the potential to serve as a soil conditioner, an adsorbent, or be used in other applications. However, there are still issues with its physicochemical properties that limit its performance. Generally, for good-performing hydrochar, additional treatment steps are required to modify the surface structure and chemical properties [4].

In previous studies, physical and chemical methods were used to modify various char products [21–24]. For instance, the surface areas of hydrochar produced from waste biomass, such as sunflower (*Helianthus annuus*) stem, walnut (*Juglans regia*) shells and olive (*Olea europaea*) stone, were increased following activation in carbon dioxide which consequently improved its absorbent ability [23]. Moreover, Zhu et al. [25] reported that the surface area of hydrochar can be modified through radiation to increase its absorption capacity. In the present study, we focused on the aging method with the aim of tailoring the surface structure and chemistry. This method offers several advantages, including lower costs, preventing or minimizing pollutant gas emissions, and limiting the generation of chemical waste. Hydrochar is known to age naturally when in contact with air, soil, and microbes [26]. Microbes were used to accelerate the biochar aging process during which oxygen-containing functional groups were increased as a result [27]. Moreover, biochar can be subjected to freeze–thaw aging to improve the surface area and absorption capacity [28]. There is a lack of studies on the aging of hydrochar to date particularly with regard to improving its physicochemical properties and surface structure. The aging method is considered promising for revealing the full potential of hydrochar because of the energy-saving and eco-friendly benefits generated by the production of hydrochar and aging it. Therefore, this study first time proposes a

comparison of the effects of water washing, microbial aging, and freezing-thawing aging on the physical and chemical properties of hydrochar as well as their impact on seed germination. It is expected that microbial hydrochar (MHC) will exhibit the best performance, as the surface porosity and physicochemical properties of biochar were enhanced by microbial activities [26].

Coffee is one of the most popular and widely consumed beverages in the world with a production of up to 9542 tons in 2018 [29]. However, coffee production also generates a large amount of coffee grounds which if not properly disposed of can result in environmental burdens. The hydrochar used in this study was derived from coffee (*Coffea arabica*) grounds as an environmentally sustainable approach to managing this waste product to obtain better properties of hydrochar and facilitate its application in horticultural production. This study aims to ascertain the effect of three pre-treatment methods (water washing, microbial aging, and freezing-thawing aging) on the surface structure and the physicochemical properties of fresh hydrochar as well as the effects of these aging methods on kale seed germination and root development.

2. Materials and Methods

2.1. Location and Materials

The study was conducted in the Department of Engineering and the Department of Plant, Food, and Environmental Sciences, Faculty of Agriculture, Dalhousie University, Canada (45.37°N, 63.26°W). Hydrochar was prepared from coffee (*Coffea arabica*) grounds obtained from Tim Hortons in Truro, NS, CA. There were four hydrochar materials used in this study as follows: fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial-aged coffee grounds hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC). Garden Club sheep manure compost was purchased from Canadian Tire Corporation, Truro, NS, Canada. Kale seeds were purchased from Halifax Seeds Company (Halifax, NS, Canada).

2.2. Hydrochar Production

The hydrothermal carbonization experiment was carried out in a stainless-steel autoclave (Parr Instrument, 4590 microreactor (Moline, Illinois, USA)) fitted with an A2140HC stirring mechanism and a 4848-reactor controller. Coffee grounds (70 g) and 280 mL of distilled water were transferred to the reactor and then sealed. The sealed reactor was positioned into the autoclave support stand and purged using nitrogen gas and then re-pressurized to 1 MPa. Inductive heating was applied to the reactor at 210 °C for 1 hr while stirring. Once the reaction was completed, the reactor temperature was cooled down to room temperature (approximately 25 °C) using a water bath. Following this, the gas in the reaction vessel was vented. The reactor was opened following filtration process to separate the hydrochar solid and the process water. The hydrochar was oven dried at 105 °C for 12 h. Finally, the dried hydrochar and process water were collected in containers and stored in shaded areas for future use.

2.3. Aging of Hydrochars

The hydrochar materials were aged according to the following procedure. To make WHC, fresh hydrochar material and distilled water were poured into a container with distilled water at a 1:10 hydrochar/distilled water ratio. The mixture was washed well and stirred continuously for 1 hr. The assumption was that washing with distilled water will leach out hydrophilic phytotoxic compounds from the hydrochar to improve its efficacy on plants [12,20]. The WHC was obtained by filtration and air dried. With respect to MHC, 1 L of distilled water was mixed with 200 g of sheep manure compost and stirred for 24 h at 2000 rotations per minute using a DLM186X1 Isotemp stirring plate (Fisher Scientific Inc., Markham, ON, Canada). The assumption was that manure compost like any other compost is rich in a beneficial microbiome that can be used to inoculate growing medi

substrates to benefit plants as recently reported by Abbey et al. [30]. To inoculate FHC with microbial tea, dried 3 kg FHC was mixed with 2.4 L of microbial tea in a plastic container at 80% moisture content for 45 days in the shaded area. To maintain moisture, the container was positioned away from light and covered with a thin film. Upon completion of the microbial-aged process, the MHC material was air dried and then stored in a sealed container. FTHC was prepared by mixing 3000 g fresh hydrochar with 2400 mL microbial tea at 80% moisture content. The mixture was then kept in the freezer (−15 °C) for 5 h followed by 19 h in a 25 °C room cycle for 45 days. After the inoculation, the FTHC was air dried and stored in a sealed container. The assumption was that the hydrochar particles disintegrate by the process of freezing and thawing leading to the creation of larger surface areas for nutrient adsorption and more active sites for microbiome activities [31,32].

2.4. Hydrochar Physical Properties

2.4.1. Bulk Density

The bulk density of the hydrochar samples was determined using a modified method as described by Kalderis et al. [33]. Briefly, hydrochar material was transferred and filled into a 50 mL laboratory tube followed by tapping the tube three times to compact the volume. The tube was then refilled to 50 mL with hydrochar material. The weight of the hydrochar material and tube was measured using an electronic MXX-412 Denver precision balance (Denver Instrument Company, CO, USA) with four replications. The bulk density (1) of the hydrochar sample was determined using the following equation:

Bulk density (g/mL) = $\frac{M_t - M_b}{V_t}$, M_t is total mass of tube and hydrochar, M_b is mass of empty tube, and V_t is the volume of tube (50 mL).

2.4.2. Porosity and Water Holding Capacity

The total porosity and water-holding capacity were determined by the methods described in Lipiec et al.[34]. All determinations were performed quadruplicated. A 50-mL hydrochar sample was transferred to a plastic cell holder with two drainage holes at the bottom. The cell holder with the hydrochar was put on a plastic tray that was half filled with distilled water to saturation for 6 h. The weight of saturated hydrochar and dry hydrochar were recorded and the total porosity (2) was determined as follows:

Porosity (%) = $\frac{M_s - M_d}{V_t}$, where M_s is the weight of saturated hydrochar, M_d is the weight of dry hydrochar, and V_t is the volume (50 mL).

The water-holding capacity measurement was carried out using the gravitational water method. The saturated cell holder was drained naturally for 24 h under gravity and the weight of the drained hydrochar was recorded. The following formula was used to determine the water holding capacity (3):

Water holding capacity = $\frac{M_a - M_d}{M_d}$, where Ma is the weight of hydrochar material after drained, and M_d is the weight of dry hydrochar material.

2.5. Surface Morphology

Scanning electron microscope analysis (SEM) measurements were made to determine the changes in surface morphology and microstructure of hydrochar samples at the Department of Mechanical Engineering, Dalhousie University. Hydrochar samples were sputter coated with a 21-nm thickness layer of Au/Pd 80/20 to prevent charging during observation. The SEM analysis was then conducted with scanning electron microscopy (SEM) (Zeiss Sigma 300 FESEM Oberkochen, Germany) at an acceleration voltage of 10 kV. The weight percent of surface elements of hydrochar samples were analyzed by an energy dispersive X-ray fluorescence spectroscopy (EDS) (Oxford Instruments Inc, Abingdon, UK).

The surface areas of hydrochar samples were determined by using Gemini II—2375 BET (Brunauer-Emmett-Teller) analyzer (Micromeritics Inc., Norcross, GA, USA) at Department of Physics and Atmospheric Sciences, Dalhousie University. The method of Brunauer–Emmett–Teller (BET) was used to determine the surface areas with N_2 adsorption at 77 K. The determination was replicated three times.

2.6. Fourier Transform Infrared (FTIR)

The variation of functional groups after hydrochar samples were analyzed by Fourier transform infrared (FTIR) at the spectral range of 4000 cm^{-1} to 500 cm^{-1}. FTIR analysis was carried out in a PerkinElmer FTIR spectrometer (PerkinElmer Inc., Shelton, USA) in the Department of Engineering, Dalhousie University Agriculture Campus. A total of 5–10 mg of hydrochar samples were positioned on the diamond surface and pressed against a metal rod and all the spectra were recorded from 64 scans at 4 cm^{-1} resolution.

2.7. Hydrochars Chemical Properties

The pH, total dissolved solid (TDS), salinity, and electric conductivity (EC) of hydrochar samples were determined with a multifunctional EC 500 ExStik pH metre (EXTECH Instrument, Nashua, USA). Briefly, 5-g hydrochar samples were mixed with 50 mL deionized water resulting in 1:10 mass/water ratio and thoroughly stirred for 1 hr using DLM1886X1 Isotemp stirring plate (Fisher Scientific Inc., Markham, ON, Canada). Finally, the hydrochar leachate was obtained by vacuum filtration for pH/TDS/salinity/EC measurement. The hydrochar leachate was also used for pouch seed germination test. All analyses were performed in triplicate.

2.8. Seed Germination Bioassay

One-way analysis was conducted in the Compost and Biostimulant Laboratory at Dalhousie University Agriculture Campus to investigate the effect of hydrochar leachates on kale seed germination and root growth using a modified method described by Islam et al. [35]. Fifteen kale seeds were placed evenly and carefully in a 16.5 × 18 cm CYG germination pouch (Mega International, USA) followed by treatment with 25 mL of hydrochar leachate. After that, the pouches were incubated in the dark at 22 °C for 2 days after which they were transferred to a growth chamber with at approximately 71% relative humidity, 25°/20 °C day/night temperature regime, and 16/8 h day/night LED lighting. The pouch assay was designed in a completely randomized design (CRD) with three replications. Each pouch added 15 mL of leachate to maintain adequate moisture for seed growth every two days. For the next seven days, the number of germinated seeds was recorded daily. Germination is generally considered to have occurred when the radicle emerges at approximately 2 mm in length. Germination rate (GR (4)), germination index (GI (5)), germination energy (GE (6)), and seed vigour index (SVI (7)) were also determined. On day 9, the kale seedlings were gently removed from the pouch and placed in the plastic tray of STD4800 Epson Perfection V850 Pro Scanner (Regent Instruments, QC, Canada) and WinRHIZO™2000 software was used to detect the morphology of kale seedlings (root length and root surface area). Germination rate and other relative germination indices were calculated using the following equations [36,37].

$$\text{Germination rate (GR)} = \frac{\text{number of seeds germinated}}{\text{total number of seeds}} \times 100$$

$$\text{Germination energy (GE)} = \frac{\text{number of seeds germinated}}{\text{number of total seeds per treatment after germination for 4 days}} \times 100$$

Germination index (GI) = $\sum$ (Gt/Tt), where Gt is the germinated numbers on day t, and Tt is the number of days.

$$\text{Seed vigour index (SVI)} = \text{Germination rate} \times \text{seedlings length}$$

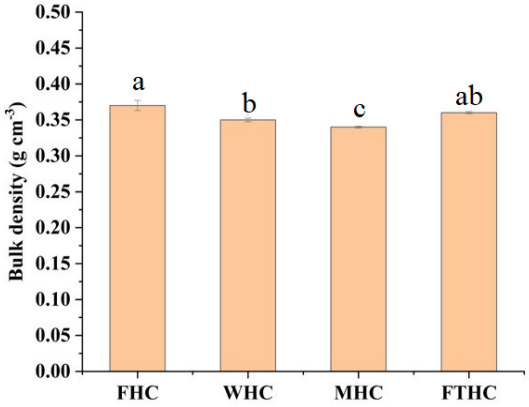
2.9. Statistical Analysis

Analysis of variance was performed to determine differences in the treatments at a significantly different level of 5%. Tukey's test was used to compare and separate the treatment means when the ANOVA suggested $p \leq 0.05$. All statistical analyses were performed using Minitab software version 20 (Minitab Inc., State College, PA, USA). All graphs were drawn by Origin Pro 8.5 0 (Northampton, MA, USA).

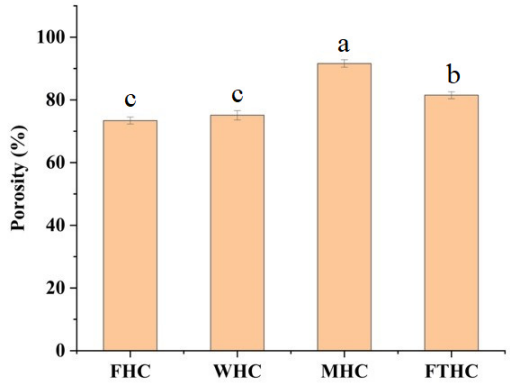
3. Results

3.1. Effect of Different Pre-Treatment Methods on Physical Properties of Hydrochar

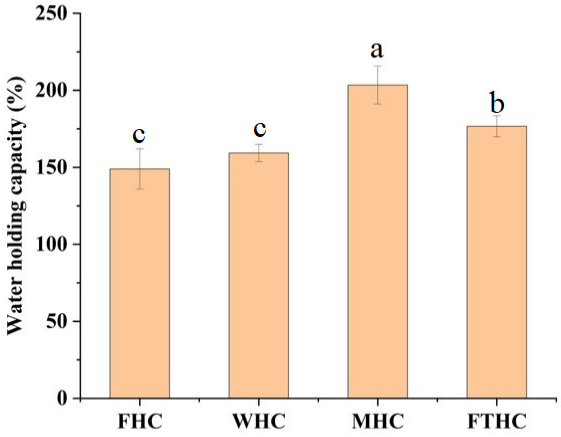
The effects of aging on hydrochar physical properties are shown in Figure 1. The difference in the letter indicates that the treatments differ significantly ($p < 0.05$). Among all modified hydrochars, MHC showed the most significant ($p < 0.05$) changes in physical properties. Compared to the control, MHC exhibited an 8.1% decrease in bulk density (0.37 to 0.34 g cm^{-3}), a 24.8% increase in porosity (73.36% to 91.64%), and a 36.4% increase in water-holding capacity (148.96% to 203.39%). The porosity and water-holding capacity of FTHC also increased significantly ($p < 0.05$) but were slightly inferior to MHC with increases of 11.3% and 18.6%, respectively, compared to FHC. Moreover, WHC showed a significant ($p < 0.05$) decrease in bulk density which decreased from 0.37 g cm^{-3} to 0.35 g cm^{-3}, representing a 5.4% decrease. The porosity and water-holding capacity of WHC also increased, by 2.32% and 6.93%, respectively, but this was not statistically significant ($p > 0.05$).



(**a**)



(**b**)



(**c**)

Figure 1. Physical properties of hydrochar are subjected to different aging processes ((**a**): Bulk density, (**b**): Porosity, (**c**): Water-holding capacity). Values represent the mean of four replicate analyses. Error bars represent standard deviation. Statistical difference between treatments is represented by lower-case letters. Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC). ((**a**): Bulk density; (**b**): Porosity; (**c**): water-holding capacity)

3.2. Effect of Different Pre-Treatment Methods on Morphological Characteristics of Hydrochars

As shown in Figure 2, the SEM images revealed that the morphology of hydrochar aged in various ways changed to varying degrees. The surface morphology of WHC and FHC appeared identical. On the surfaces of FHC and WHC, we can clearly observe compact structures and smooth surfaces with small-diameter pores. In contrast, the surface morphologies of MHC and FTHC were dramatically altered (Figure 2). The surfaces of MHC and FTHC were rough and exhibited larger regular network structures compared to FHC and WHC. In addition, it was evident that MHC and FTHC had more pores with well-developed structures than FHC.

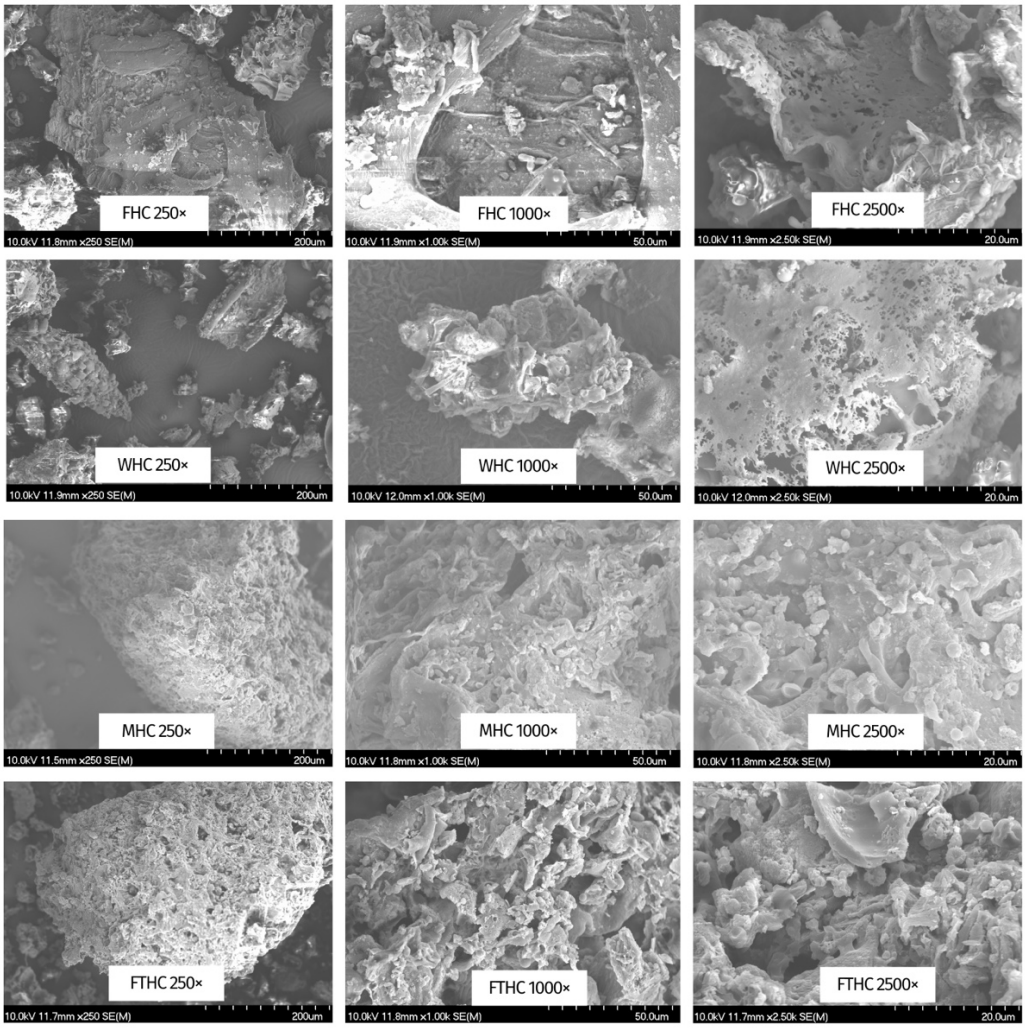


Figure 2. Scanning electron microscope (SEM) images of fresh hydrochar (FHC), water washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC) with magnifications of 250×, 1000×, and 2500×.

By employing an X-ray fluorescence spectroscopy (EDS) investigation, the elemental surface composition and dispersion of hydrochars were determined (Table 1). The EDS examination revealed that the primary elements were carbon (C), nitrogen (N), and oxygen (O). The C, N, and O percentages in FHC were 76.8%, 5.9%, and 17.3%, respectively. Compared to those of FHC, the weight of WHC elements was marginally altered. Compared to FHC, N, and O in MHC increased from 5.9% to 8.4% and 17.3% to 22.2%; FTHC, N, and O content increased to 6.9% and 21.1%, respectively. Furthermore, microbial and freezing–thawing aging resulted in a decrease in the C content from approximately 77% to 69% for MHC and from 77% to 72% for FTHC (Table 1).

Table 1. Hydrochar carbon (C), nitrogen (N), and oxygen (O) contents as affected by different aging techniques.

Element	FHC	WHC	WHC	FTHC
C	76.8	75.7	69.3	72.1
N	5.9	5.9	8.4	6.9
O	17.3	18.4	22.4	21.1

Note: Carbon (C), Nitrogen (N), Oxygen (O), Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC).

Based on the BET analysis, the hydrochars experienced a remarkable change in surface area after aging (Figure 3). Overall, the trend of BET surface area of hydrochars was MHC > FTHC > WHC = FHC. The BET surface area of FHC was 0.59 m^2 g^{-1}. As expected, the BET surface areas of MHC and FTHC were increased by 3.2-fold and 2.4-fold, respectively, compared to FHC with the values of 2.46 m^2 g^{-1} and 1.99 m^2 g^{-1}.

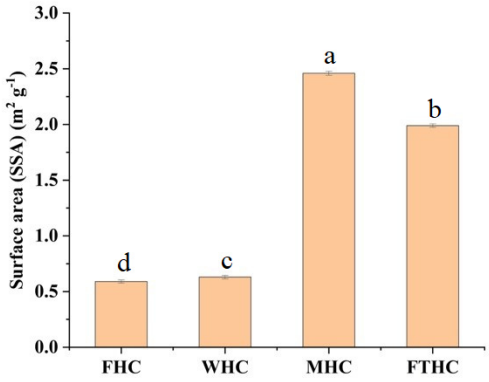


Figure 3. BET analysis of the hydrochar derived from coffee grounds with different modification methods. Fresh hydrochar (FHC), water−washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing−thawing aged hydrochar (FTHC). Error bars represent standard deviation.Statistical difference between treatments is represented by lowercase letters.

3.3. FTIR analysis of Hydrochars

The surface functional groups of the hydrochars were identified by FTIR as expressed in Figure 4. Overall, there was no clear change in the major absorption peaks of the four hydrochar samples, but their intensities were different. The peak of 3345 cm^{-1} was attributed to the O-H stretching vibration [38]. The peaks at 2928 cm^{-1} and 2870 cm^{-1} were attributed to aliphatic C-H stretching vibration peaks [39]. The peaks in 1700–1630 cm^{-1} and 1457 cm^{-1} were attributed to increased C=O (carbonyl, Quinone, ester, or carboxyl) functions and C=C vibrations, respectively [40]. The peak at 1039 cm^{-1} was ascribed to C-O stretching vibration [38]. The peak at 1171 cm^{-1} was attributed to the C-C stretching vibration [41].

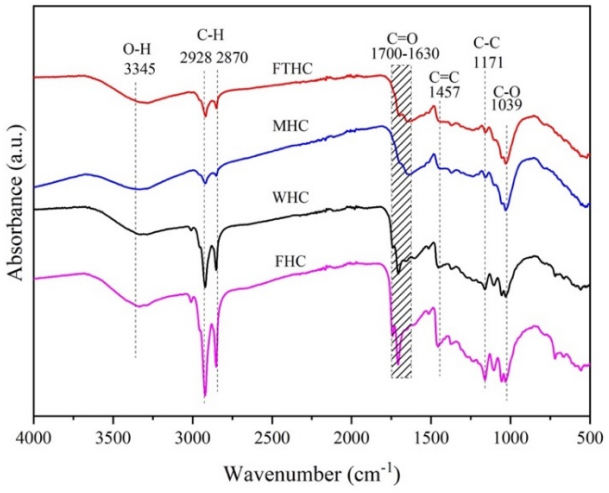


Figure 4. FTIR spectrum of hydrochars subjected to different aging processes. Fresh hydrochar (FHC), water−washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing−thawing aged hydrochar (FTHC).

3.4. Effect of Pre-Treatment Methods on the Chemical Properties of Hydrochar

The chemical properties of the hydrochars were significantly affected ($p < 0.05$) by the different aging methods as shown in Figure 5a–d. As seen in Figure 5a, the pH of all the modified hydrochars increased to varying extents, ranging between 4.1 and 5.8, with the highest increase observed in MHC followed by FTHC and then WHC. The pH of MHC increased by approximately 42%, reaching 5.8, compared to FHC. Similarly, there was a noticeable increase in the pH of FTHC which was approximately 39% higher at 5.7 than that of FHC. Comparatively, a clear pattern was observed for EC, salinity, and TDS of the hydrochars (Figure 5b–d). WHC had the lowest TDS at 126.9 compared to FHC, WHC, MHC, and FTHC. Additionally, MHC significantly ($p < 0.05$) reduced EC, salinity, and TDS by approximately 33%, 35%, and 33%, respectively, compared to FHC. FTHC showed the smallest reduction in EC, salinity, and TDS at 27%, 22%, and 21%, respectively, compared to FHC.

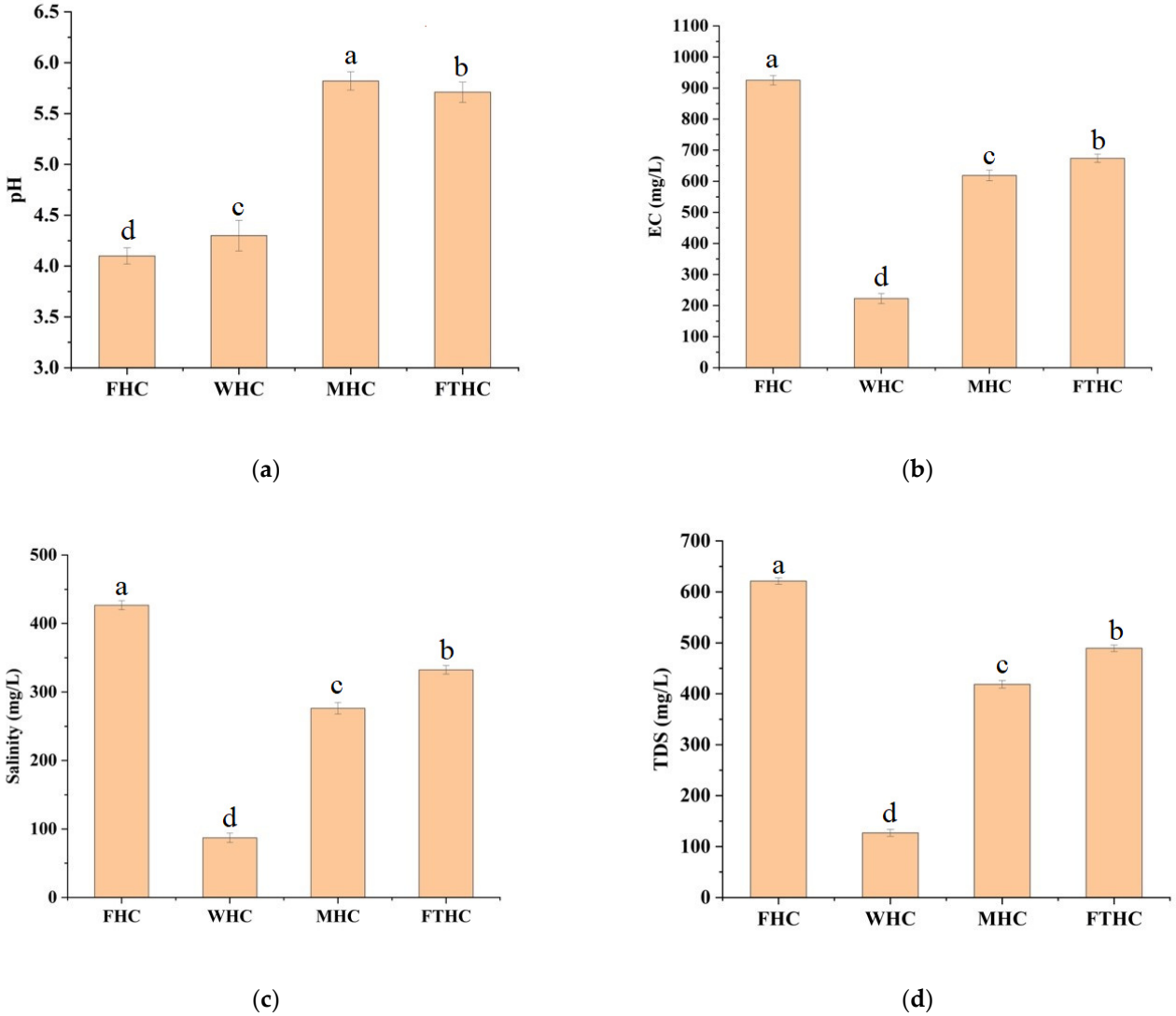


Figure 5. Chemical properties of hydrochar under different modification methods: (**a**) pH, (**b**) electrical conductivity (EC), (**c**) salinity, and (**d**) total dissolved solids (TDS). Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC). Values represent mean of three replicate analyses. Error bars represent standard deviation. Statistical difference between treatments is represented by lower-case letters.

3.5. Effects of Aged Hydrochars on Seed Germination Indices

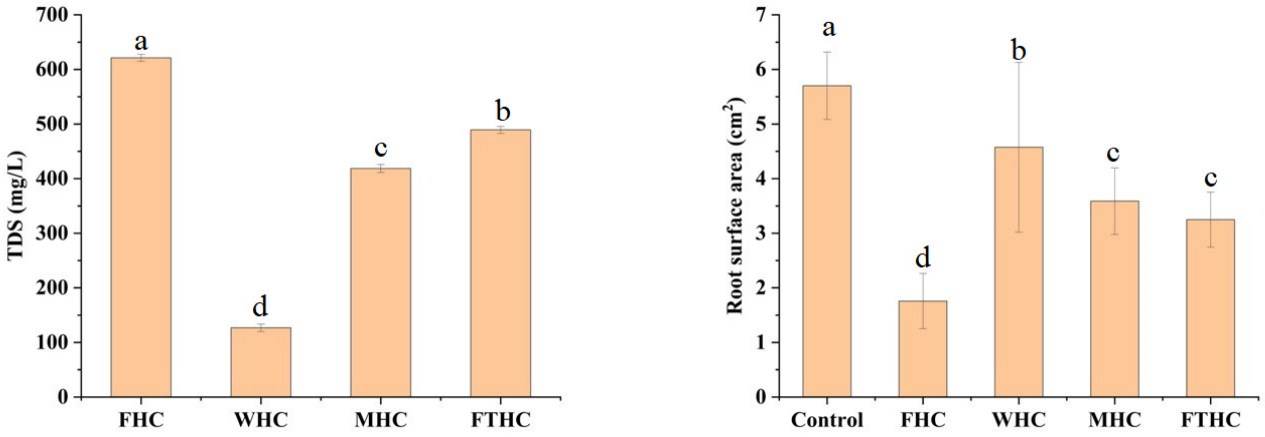
The overall trend for seed germination rate was MHC > control > FTHC > WHC > FHC (Table 2). FHC had the least average germination rate that significantly ($p < 0.05$) different from the other aged hydrochars. In addition, germination energy (GE), germination index (GI), and seed vigour index (SVI) were used to determine seedling growth response. As shown in Table 2, the control treatment had the highest GE, GI, and SVI, respectively.

Table 2. The average germination rate (%), germination energy (%), germination index, and seed vigour index of kale (*Brassica oleracea var.* sabellica) treated with different hydrochar leachates.

Treatment	Germination Rate (%)	Germination Energy (%)	Germination Index	Seed Vigour Index
Control	82.2 ± 10.18 ab	64.4 ± 0.20 a	13.49 ± 3.16 a	9.02 ± 2.76 a
FHC	28.9 ± 19.20 c	6.7 ± 0.07 b	2.52 ± 1.54 c	1.49 ± 1.10 c
WHC	68.9 ± 10.18 b	40.0 ± 0.12 ab	9.17 ± 1.36 b	6.90 ± 1.83 bc
MHC	86.7 ± 17.60 a	48.9 ± 0.14 ab	11.81 ± 2.77 ab	7.13 ± 2.40 ab
FTHC	71.1 ± 10.18 ab	46.7 ± 0.24 ab	10.17 ± 2.33 ab	5.31 ± 1.07 b
p-value	0.004	0.018	0.002	0.009

Statistical difference between treatments is represented by lower-case letters. Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC).

Effects of hydrochar treatments on kale seed root development as shown in Figures 6 and 7. The control showed the best root development, while a significant ($p < 0.05$) inhibition of root development was observed for FHC. Moreover, the three pre-treatment methods significantly reduced the inhibitory effect on root development compared to FHC. Among them, WHC had the smallest inhibitory effect with a root length and root surface area of 5.7 cm and 3.6 cm², respectively.



(**a**) (**b**)

Figure 6. (**a**) Root length and (**b**) surface area of kale (*Brassica oleracea var.* sabellica) seedlings treated with different hydrochar leachates. Values represent mean of seven replicate analyses. Error bars represent as standard deviation. Statistical difference between treatments is represented by lower-case letters. Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC). Error bars represent standard deviation. Statistical difference between treatments is represented by lower-case letters.

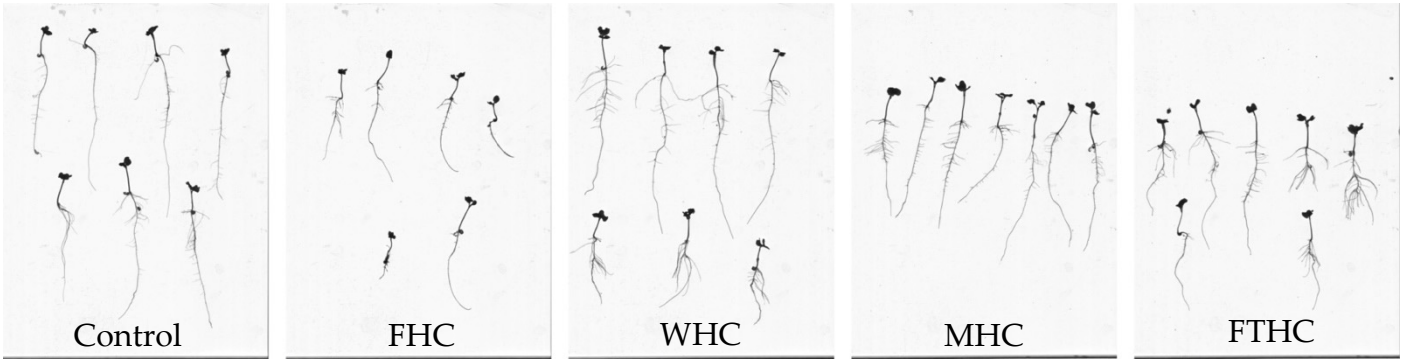


Figure 7. Photo comparison of seedlings showing differences in size of kale (*Brassica oleracea* var. sabellica) as affected by different hydrochar leachates. Fresh hydrochar (FHC), water-washed hydrochar (WHC), microbial aged hydrochar (MHC), and freezing–thawing aged hydrochar (FTHC).

4. Discussion

4.1. Explanation for Physical Properties Changes

Water-holding capacity is an important soil indicator that affects soil health and soil quality [42]. Due to the porous structure of hydrochar, people have been exploring the use of hydrochar for improving the soil's physical properties [43]. Meanwhile, researchers have conducted a series of studies to optimize hydrochar and improve its pore structure [44,45]. In this study, MHC displayed the greatest changes in physical properties and was consistent with previous hydrochar modification studies [23,25]. This may be attributed to the structural changes in hydrochar caused by microbial degradation as the surface area increased [46]. Specifically, during microbial aging, the dissolved organic carbon (DOC), inorganic components, and some tar residues in the surface of hydrochar carbon skeleton are degraded which leads to an increase in the surface area and porosity of the hydrochar [46]. For FTHC, changes in physical properties can be associated with the freezing–thawing aging process; according to Liu et al. [47], after 20 times of freezing and thawing cycles, the porosity of biochar increased by 3.2% which resulted in improved water-holding capacity. However, it is important to note that the FTHC aging process also involves microbial activities (microbial tea was added); surprisingly, the physical properties of FTHC after freezing–thawing and microbial activities were slightly inferior to those of MHC (Figure 1). It is speculated that the improvement of the physical properties of FTHC was mainly due to the freezing–thawing process because the low temperature of FTHC during the aging period inhibits microbial activity [48]. There have been few studies conducted on the effects of washing on the physical properties of hydrochar. We speculate that the decrease in bulk density in the WHC could be attributed to washing off the ash on the surface of hydrochar. Overall, our results suggest that modified hydrochars, particularly MHC, are more effective for improving soil water retention and overall soil health.

4.2. Explanation Explanation for Surface Characteristics Changes of Hydrochar

In this study, the decrease in C content in MHC could be attributable to the effects of microbial digestion [40]. In addition, earlier research conducted by Jing et al. [49] demonstrated a reduction in the C content of hydrochar after freezing and thawing. As a result of carbon loss, the O and ash contents of the samples increased relatively after aging which is consistent with the results of this experiment. The increase in the O content in hydrochar means an increase in the hydrophilic oxygen functional groups which subsequently enhances the hydrophilicity of hydrochar [50]. The increased hydrophilicity of hydrochar implies improved wettability [33] which is a favorable attribute for its application as a soil amendment. Hydrophilic hydrochar can enhance the water-holding capacity of soils and increase the availability of nutrients [51]. The increased N content of MHC could be related to the effect of microbial activity [52]. However, Wang et al. [40]

also reported that when a hydrochar produced at 260 °C was aged in soil for 4–16 months, its O and N content decreased while its C content increased. The differences in results may be due to variations in the length of the aging period and the types of soil used in the study. The increased N content of FTHC could be attributed to the freezing–thawing process. In a recent study by [53], they observed that the freezing–thawing process increased the amount of inorganic N in soils by 1.67–26.77 times. Additionally, Dalias et al. [54] suggested that microbial activity and soil N cycling were inhibited at lower temperatures. Therefore, we hypothesized that freeze–thaw cycles will alter the physiochemical properties and microbial activities of the hydrochar. According to a prior study carried out by Sun et al. [55], hydrochar could be regarded as an effective adsorbent since it contains more O and less C. The present study, therefore, provides additional evidence that MHC and FTHC have a superior adsorption capability.

A recent study showed that after microbial aging for 60 days, the surface area of the hydrochar increased by 2.2-fold compared to fresh hydrochar [46]. This is consistent with the results of our study. The increase in microbial-aged hydrochar BET surface area was associated with the release of dissolved organic matter on the surface of the hydrochar. During the microbial aging process, hydrochar loses an extensive amount of decomposable and soluble organic and inorganic components which leads to an increase in surface area [46,56]. The BET surface area of FTHC was 1.99% m^2 g^{-1} with a 2.4-fold increase over FHC. As pointed out by a previous study [57], the infiltration of water leads to swelling followed by the shrinking of pores of hydrochar due to temperature changes, thus breaking the surface of the hydrochar and increasing the surface area further. It is worth noting that an excessive number of freezing–thawing cycles can also damage biochar particle size and gradual loss of water-holding capacity, resulting in a reduction in particle size due to the expansion of micropores [47]. Thus, future research should determine the optimal number of freeze–thaw cycles and monitor the long-term water-holding capacity of hydrochar after freeze–thaw treatment. The increase in surface area of MHC and FTHC was also confirmed in the SEM analysis (Figure 2), and the rough surface of MHC and FTHC helps to enhance the surface area. It was also observed that the BET surface area of WHC increased by approximately 7.6%. It can be speculated that the ash produced in the HTC process was washed off the WHC-aged hydrochar leading to an increase in its surface area. According to Sun et al. [55], the surface area plays an important role in determining the adsorption capacity of hydrochars, therefore, it can be concluded that MHC and FTHC have better adsorption capacity.

We observed that there was a considerable difference in the intensity of the peaks at 2920, 2870, and 1171 cm^{-1}. FHC exhibited the highest intensity which indicated fresh hydrochar exhibited a higher abundance of C-H/C-C. The weak intensity of the other three hydrochar samples could be attributed to carbon (C) removal [25]. Compared with FHC, the peak at 1039 cm^{-1} illustrated that those aging methods could proliferate O-containing functional groups (C-O). At peaks of 1700–1630 cm^{-1}, the peaks became wider and shifted to the right (1648 cm^{-1}) which indicated that the aging process may lead to the breakage of the C=O functional groups. The shift of peak at 1700 cm^{-1} can be ascribed to the deprotonation of acid functional groups, such as carboxylic acid to carboxylate, per the increase in the pH of MHC and FTHC. Furthermore, the increased microbial abundance and activities might have further improved the contents of amide bonds leading to the observed differences in addition to the observed increase in N contents of the MHC and FTHC treatments.

4.3. Seeds Germination Indices

Bargmann et al. [20] reported that hydrochar inhibited cress (*Lepidium sativum*) germination which is consistent with our experimental results. Their study identified organic acids and phenols as phytotoxic compounds in hydrochar, an area that requires further attention in future research. Chemical analysis of hydrochar showed that FHC had a lower pH and the highest EC which could disrupt the balance between soil water and

soil nutrients, affecting plant growth [58]. Bargmann et al. [20] also found that water-washing hydrochar greatly reduced the negative impact on germination, as the phytotoxic compounds in hydrochar are mostly water-soluble (phenols). In our experiment, WHC had a considerably improved germination rate and root development compared to FHC but still showed an inhibitory effect compared to the control. Therefore, future research should investigate different washing ratios and washing times.

MHC and FTHC showed some alleviation of inhibition on seed germination which may be related to the effect of aging on the chemical properties of hydrochar. According to Msimbira and Smith [59], the optimal pH range for plant growth is between 5.5 and 6.5 as most mineral nutrients are available within this pH range. The rise in MHC pH could be due to the decomposition of acidic organic molecules by microbes during the aging process as previously reported by Yu et al. [12]. Furthermore, Roehrdanz et al. [3] mentioned that microbial degradation may reduce harmful substances. The surface area and porosity of hydrochar are increased after microbial aging [46] which, in turn, enhances its adsorption capacity, allowing for the adsorption of phytotoxic compounds and reducing their inhibitory effect. On the other hand, the increase in surface area and porosity provides more space for microorganisms to degrade harmful components in the hydrochar, ultimately resulting in a reduction in hydrochar's phytotoxicity and its inhibitory effect on plant germination and growth [46,60]. Our study also found that MHC had the highest germination rate, but its root development was not particularly good compared to the control and WHC. This could be attributed to seed germination and seedling growth being two distinct physiological stages [24]. Additionally, FTHC showed a noticeable increase in pH of approximately 39% compared to the control, contradicting the findings reported by [56,57]. This increase in pH may be related to the addition of micro-tea. MHC and FTHC were more suitable as soil amendments than FHC and WHC due to their low acidity levels. Further research is needed on the effect of microbial or freezing–thawing aging on the salinity, EC, and TDS of hydrochar. There is currently no report on the effect of freezing–thawing aging on seed germination, and we can speculate that the reduced inhibitory effect of FTHC may be related to the microbial activities in micro tea. Overall, the seed germination experiment confirmed the inhibitory effect of FHC on kale seed germination, and both washing and aging alleviated this inhibition to varying degrees.

5. Conclusions

Hydrochar exhibits considerable promise as a soil amendment and absorbent in agricultural and remediation applications. This study is the first to evaluate and compare the influence of three pre-treatment methods on hydrochar with a focus on alterations in its physical and chemical characteristics as well as its impact on kale seed germination. The findings indicated that overall, the three pre-treatment methods have different degrees of effectiveness in enhancing the physicochemical properties of hydrochar with the most notable improvements observed in MHC. FHC exhibited a significant inhibitory effect on seed germination, while MHC showed the highest germination rate, highlighting its potential as a soil amendment. The improvement in the physicochemical properties of MHC and the reduction in its inhibitory effect can be attributed to microbial degradation. However, it is important to note that the modified hydrochars still have inhibitory effects on seed germination and root development. In summary, the study suggests that pre-treated hydrochar, especially hydrochar under microbial aging, has considerable potential as a horticultural substrate.

Future research suggestions are as follows:

1. Further studies should use X-ray diffraction (XRD) and thermogravimetric analyzer (TGA) to analyze the properties of hydrochar.
2. To completely eliminate the inhibitory effect, further optimization of the aging conditions is necessary.

3. Plant growth experiments are needed to validate the impact of modified hydrochar on plant growth.

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