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Characterization and Greenhouse Trial of Zn Bio-Chelates Derived from Spent Coffee Grounds

Ana Cervera-Mata [1], Leslie Lara-Ramos [2], José Ángel Rufián-Henares [3,*], Alejandro Fernández-Arteaga [2], Jesús Fernández-Bayo [4] and Gabriel Delgado [4]

[1] Department of Soil and Water Conservation and Organic Waste Management, CEBAS-CSIC, Campus Universitario de Espinardo, 30100 Murcia, Spain; agcervera@cebas.csic.es
[2] Department of Chemical Engineering, University of Granada, 18071 Granada, Spain; lara.ramos@gmail.com (L.L.-R.); jandro@ugr.es (A.F.-A.)
[3] Department of Nutrition and Bromatology, University of Granada, 18071 Granada, Spain
[4] Department of Soil Science and Agricultural Chemistry, University of Granada, 18071 Granada, Spain; jdfbayo@ugr.es (J.F.-B.); gdelgado@ugr.es (G.D.)
* Correspondence: jarufian@ugr.es

Abstract: The conversion of spent coffee grounds (SCG) into hydrochars has been the subject of extensive research in recent years, aimed at evaluating their potential for biofortifying foods and mitigating the plant toxicity linked to SCG. This study aimed to assess the physicochemical characterization and the impact of incorporating both activated (ASCG and AH160) and functionalized SCG (ASCG-Zn), as well as SCG-derived hydrochars (AH160-Zn), on cucumber yield and plant zinc content. The following physicochemical properties were analyzed: specific surface area, pH and electrical conductivity, polyphenols, and nuclear magnetic resonance. The by-products activated and functionalized with zinc were applied to cucumber crops grown in a greenhouse across multiple harvests. The activation of both SCG and H160 reduced the specific surface area of the particles. However, when these by-products were functionalized, their Zn content increased significantly, up to 7400 ppm. Concerning polyphenol content, the activated products showed levels ranging from 3.5 to 4.9 mg GAE/g. Regarding cumulative production, the treatments that showed the highest yields were the by-products activated and functionalized with Zn reaching 25 kg. Incorporating these by-products notably raised the Zn content in cucumbers, reaching 0.1 mg Zn per 100 g of fresh weight. The activated by-products demonstrated the highest Zn utilization efficiency.

Keywords: biofortification; OH-activation; by-products; cucumbers; ecological production

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1. Introduction

Various strategies have been used to address micronutrient deficiencies in human nutrition. Hidden hunger is described as the presence of micronutrient deficiencies in the absence of an energy deficiency, affecting 2 billion people worldwide [1]. In humans, Zn deficiency is due to a low concentration of this micronutrient in the diet, which in turn is related to Zn deficiency in soils [2]. Zinc deficiencies commonly occur in calcareous (high pH) soils that have been levelled by machinery for uniform irrigation. This is because levelling, particularly in calcareous soils, removes the topsoil and organic matter, which are rich in micronutrients [3]. These soils are typically sandy, calcareous, and saline, with elevated levels of organic matter, nitrogen, and phosphorus [2]. According to Adriano et al. [4], the available Zn in soils constitutes between 1.4% and 8% of the total Zn content.

There are many methods to increase the Zn content in plants. One of them is agronomic biofortification, which include commercial chelates, such as diethylenetriamine pentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and ethylenediamine-N, N′-bis (2-hydroxyphenylacetic acid) (EDDHA), as well as salts [5,6]. However, other strategies for increasing Zn in soils include the use of organic amendments, though a recent article

indicates that a decade of applying these amendments does not enhance the bioavailability of this micronutrient in crops [7]. Therefore, one of the recently used alternatives has been the use of Zn-functionalized organic amendments to increase this micronutrient in lettuce leaves in an in vitro trial [8].

One of the organic amendments used to increase micronutrients in plants is spent coffee grounds (SCG). Lara-Ramos et al. [8] conducted an experiment with SCG, the solid residue obtained after brewing coffee. Other second-generation products can be obtained from this by-product, such as hydrochars derived from spent coffee grounds [9]. These were characterized by having a higher amount of organic C, less P and K, and more polyphenols. The latter, along with melanoidins, have been attributed with micronutrient chelating properties, being largely responsible for the increase of micronutrients in plants [9,10]. Additionally, a polymer extracted from coffee brew (possibly melanoidins) has been described with metal chelating properties against Fe, Zn, and Cu [11,12]. However, polyphenols are also responsible for the phytotoxic effect that both SCG and hydrochars have on crops [13].

In the study of Cervera-Mata et al. [13], the effect of hydrothermal carbonization (a physicochemical treatment for generating hydrochars, HTC) was evaluated, and it was observed that the addition of hydrochar did not enhance plant growth; in fact, it had the opposite effect. The phytotoxic effect of SCG was not eliminated when SCG was transformed into hydrochars. This study also evaluated the effect of adding hydrochars on Zn content in lettuce and found no statistically significant differences compared to SCG.

Zinc biofortification has occurred in other crops, not just in lettuce, such as cowpea grains, rice, or cereals. HarvestPlus partners had launched over 140 biofortified varieties of 10 staple crops across 26 countries. In the study of Oliveira et al. [14], all cowpeas showed Zn enrichment in grains in response to $ZnSO_4$ $7H_2O$ application compared to untreated plants. In the study of Szerement et al. [15], in the highest yield grain, Zn concentrations were obtained for application of foliar 0.3% of Zn.

Another alternative to improve the absorption capacity of SCG is to use activation and functionalization techniques. Activated and functionalized SCG and hydrochars [8] have been tested to increase the content of zinc. Lara-Ramos et al. [8] found that the application of these bio-chelates reduced phytotoxicity in lettuce and increased the Zn content in plants by 318.2% when hydrochar activated and functionalized with Zn at 180 degrees was applied. This same study was previously conducted with Fe, using bio-chelates activated and functionalized with this micronutrient, obtaining very similar results [8]. Therefore, these techniques seem promising to increase the micronutrient content in plants.

Regarding physical and physicochemical properties of hydrochars, there are some studies that have delved into these characteristics. Hydrochars derived from SCG were responsible for a decrease of volatile matter (by 13.9%) with a corresponding increase in fixed C of 14.3% [16,17]. When scanning electron microscopy was applied, SCG hydrochars exhibited distinctive morphologies, indicating that the HTC process significantly transformed the surface structures of the SCG hydrochars. The enhanced porous characteristics of SCG hydrochars could facilitate better air access and distribution, leading to increased thermal reactivity during combustion [16]. Therefore, hydrochars can be used as organic soil amendments and as mobilizers of elements within the soil.

There are many studies that have used zucchini to examine the addition of organic soil amendments and assess their influence on the growth of this crop and its micronutrient content. Cucumber (*Cucumis sativus* L.), part of the Cucurbitaceae family, is primarily grown in greenhouse environments [18]. Asia leads global cucumber production, accounting for 90.1%, while Europe contributes 6%. In Spain, 8010 hectares are allocated to cucumber farming, producing 769,970 tons annually [19]. Several cultivation techniques are employed for cucumbers, with greenhouse cultivation proving especially efficient. The area devoted to greenhouse horticultural crops currently covers around 65,000 hectares [20], motivated by the demand for a year-round supply of fresh produce. Nevertheless, agricultural practices are linked to various environmental impacts, including significant greenhouse gas emissions that contribute to global warming and climate change [21].

Considering all these factors, the objectives of this study are: (i). to characterize, from a chemical and physicochemical point of view, two Zn bio-chelates derived from SCG; (ii). to test in a greenhouse trial with Dutch cucumber the capacity and efficacy of these bioproducts as Zn biofortification agents in the fruit. This would allow us to verify whether the bio-chelates derived from SCG could serve as an alternative to commercial chelates in agriculture. These objectives represent interesting advances in research with bioproducts derived from SCG. First, previous studies have only examined lettuce leaves in in vitro assays, and scaling up these products (from climatic chambers to commercial greenhouses) poses a significant research challenge. Additional benefits include reusing waste, the potential for biofortifying plants with Zn, and creating a circular economy process using a second-generation by-product such as hydrochar.

2. Materials and Methods

2.1. Bioproducts: Spent Coffee Grounds and Hydrochars

Spent coffee grounds (SCG) were collected from the cafeteria of the Faculty of Pharmacy at the University of Granada. They were spread into a thin layer and air-dried at room temperature (18–21 °C) to remove any remaining moisture. Hydrothermal carbonization (HTC) was performed in a 1-L Highpreactor™ BR-300 reactor (Berghof Ltd., Berchtesgaden, Germany), where 30 g of SCG and deionized water, at a solid-to-water ratio of 1:10 (*w*/*w*), were loaded. The temperature was set to 160 °C, with a heating time of 15–20 min, and the reaction proceeded for 1 h at 300 rpm. Once cooled, the resulting hydrochars (H160) were recovered by vacuum filtration, then dried overnight in an oven at 60 °C.

2.2. Activation and Functionalization of Bioproducts

SCG and SCG hydrochar produced at 160 °C (H160), along with their activated bioproducts (ASCG, AH160) and Zn bio-chelates (ASCG-Zn, AH160-Zn), were prepared following the activation and functionalization methodology outlined by Lara-Ramos et al. [8]. The bioproducts (SCG and hydrochars) were activated using 0.1 M NaOH at 40 °C. Zinc sulfate heptahydrate ($ZnSO_4$ $7H_2O$, Sigma, St. Louis, MO, USA) was functionalized. For each mixture, 40 g of bioproduct, 10 g of reagent, and 400 mL of deionized water were combined, then stored under dark conditions at room temperature with stirring at 120 rpm for 24 h. The mixtures were centrifuged at 2500 rpm for 10 min at 20 °C, and the supernatants were decanted. Zinc content in the bio-chelates was determined through mineralization with HNO_3 (65%) and H_2O_2 at 185 °C for 20 min using a microwave digestor (Multiwave 5000 with Rotor 24HVT50, Anton Paar, Graz, Austria). Zn contents in the extracts were measured using a PerkinElmer® Avio500 inductively coupled plasma–optical emission spectrometer (ICP-OES; Waltham, MA, USA). The final Zn contents of the bioproducts, expressed in mg kg^{-1}, were as follows: ASCG: 6.5 ± 0.5; AH160: 15.5 ± 0.1; ASCG-Zn: 11,122.7 ± 241.6; AH160-Zn: 11,798.5 ± 240.6.

2.3. Characterization of Assayed by-Products

Specific Surface Area: The Brunauer–Emmett–Teller (BET) model was employed for the analysis of specific surface area. Before this procedure, the bioproducts were dried at 120 °C for 24 h in an oven to remove residual moisture. Subsequently, they were subjected to vacuum evacuation for degassing at 120 °C for 11 h. After completing this pretreatment, the samples were analyzed using N_2 adsorption isotherms at 77 K (−196.15 °C). The procedure was carried out with a MicroActive 5.02 ASAP 2420 surface area and porosity analyzer at the Central Research Support Services (SCAI) of the University of Malaga.

pH and Electrical Conductivity: These were analyzed in a 1:10 (*w*:*v*) ratio of bioproduct to distilled water.

Total Polyphenols: The Folin–Ciocalteu method was employed to determine the total polyphenol content. Results were expressed as mg of gallic acid equivalent per gram of bioproduct (mg GAE/g). The solid samples were subjected to a prior extraction process with 70% methanol.

Nuclear Magnetic Resonance (NMR): A cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectroscopy (13C-CPMAS-NMR) was performed at the Central Research Support Services (SCAI) of the University of Jaén. The analysis was conducted using a Bruker BioSpin GmbH 500 MHz spectrometer (Rheinstetten, Germany) with 4 mm zirconium rotors at a spinning speed of 10 kHz. The parameters used were contact time of 1 ms, time between scans of 3 s, acquisition time of 20 ms, and 3000 scans.

The classification of organic carbon functional groups was conducted as described by Fernández-Bayo et al. [22] as follows: (i) aliphatic C bonded to another short aliphatic chain (0–27 ppm); (ii) aliphatic C bonded to another long aliphatic chain (27–47 ppm); (iii) alkyl-N and O C (47–113 ppm); (iv) aromatic phenolic C or phenolic ether C (113–160 ppm); and (v) carboxylic C or keto C (160–210 ppm).

Structural characterization was also performed by calculating the hydrophobicity (HB/HI), alkyl ratio (A/AO), aromaticity (ARM), and lignin ratio (LR) obtained from the organic carbon domains using the equations described by Fregolente et al. [23]:

$$\frac{HB}{HI} = \frac{\%(113-160) + \%(0-27) + \%(27-47)}{\%(27-47) + \%(47-113) + \%(160-210)}$$

$$\frac{A}{AO} = \frac{\%(0-27) + \%(27-47)}{\%(47-113)}$$

$$ARM\ (\%) = \frac{\%(113-160)}{\%(0-27) + \%(27-47) + \%(47-113)} \times 100$$

$$LR = \frac{\%(0-27) + \%(27-47)}{\%(47-113)}$$

2.4. Greenhouse Trial

The experiment was carried out in a greenhouse at the "Fundación Cajamar" Experimental Station in Almería, Spain (36°47′23″ N, 2°43′13″ W; 155 m a.s.l.) between October 2022 and January 2023. The location falls within a semi-arid subtropical Mediterranean climate, with average temperatures during the study period ranging from a low of 12.2 °C to a high of 16.1 °C. The average annual precipitation is 220.5 mm. The experimental plot measured 30 m in length and 8.5 m in width, providing a total usable area of 255 m^2.

The soil used in the experiment was previously characterized by the staff at the experimental station. According to the internal report, the soil composition was as follows: 69.79% sand, 17.57% silt, 12.64% clay, with a pH of 7.4, electrical conductivity (EC_{25}) of 2.05 dS/m, organic carbon (OC) content of 1.35%, carbonate content (as $CaCO_3$) of 29.2%, C/N ratio of 8.06, total nitrogen (N) of 0.17%, soil nitrate (NO_3^--N) of 46.05 mg/kg, and available phosphorus (P) of 318.1 mg/kg.

The bioproducts tested, at a dose of 0.2%, were ASCG, AH160, ASCG-Zn, and AH160-Zn. Two control treatments were included: untreated soil (control) and a commercial zinc chelate (control-Zn) applied at 10 mg/kg of soil. The commercial chelate, zinc ethylenediaminetetraacetate (EDTA-Zn, 14% *w*/*w*), was provided by Trade Corporation International, S.A.U. The study involved six total treatments (Table 1), arranged in a split-plot design with four replicates. Each plot contained one replicate per treatment, randomly distributed, and consisted of four plants, resulting in 16 individuals per treatment (n = 16).

The planting layout was organized with 1.5 m between crop rows and 0.5 m between plants within each row, resulting in a planting density of 1.33 plants per square meter. To apply the bioproducts, a hole measuring 20 cm deep and 15 cm in diameter (equivalent to 4 kg of soil) was dug at each planting point. The soil from all holes assigned to the same treatment was collected and thoroughly mixed with the respective bioproduct using a concrete mixer for 5 min. Each hole was then refilled with the treated soil mixture. For the control treatments, the same soil preparation procedure was followed. The commercial chelate was dissolved in distilled water and applied to the soil surface.

Table 1. Treatment details of the greenhouse experiment.

Treatment	Description
Control	No bioproduct
Control-Zn	Commercial chelate (EDTA-Zn, 14%)
ASCG	Activated spent coffee grounds
AH160	Activated hydrochar obtained at 160 °C
ASCG-Zn	Activated spent coffee grounds functionalized with Zn
AH160-Zn	Activated hydrochar obtained at 160 °C functionalized with Zn

Cucumber seedlings (*Cucumis sativus* L. var. 'Almería' cv. 'Huracán'), 21 days old, were obtained from the commercial greenhouse Acrena S.A.T 251 (Almería, Spain). Six days after soil preparation, one seedling was planted in each planting hole at a depth of 8 cm.

2.5. Crop Maintenance

The experiment was conducted under organic management, utilizing fertilizers authorized for organic farming, with irrigation applied through a drip irrigation system. Each cucumber row was irrigated using polyethylene pipes, with emitters spaced 50 cm apart and an irrigation rate of 3 L/(h·m^2). During the first 15 days following transplanting, the crop was irrigated with a nutrient solution containing 10 mM/L nitrogen (N), 1.41 mM/L phosphorus (P), and 5.56 mM/L potassium (K), derived from an organic fertilizer with a nutrient composition of 3.5% N, 2.5% P_2O_5, and 6.5% K_2O, diluted to 3.2‰.

To maintain optimal nutrient levels, the concentrations of nitrate (NO_3^-), potassium (K), calcium (Ca), and sodium (Na) in the extracted soil solution were monitored biweekly using suction probes. The nitrate concentration was maintained within the range of 3 to 10 mM/L, while the K/Ca ratio was kept between 0.5 and 1. These concentrations were measured using rapid analysis ion meters (LAQUAtwin, Horiba, Japan).

2.6. Plant Sampling and Processing

The cucumbers were harvested at three intervals: Harvest 1 (H1) was conducted 75 days after planting, when all plants had reached uniform maturity, followed by Harvest 2 (H2) and Harvest 3 (H3) at 15-day intervals thereafter. The harvested fruits were cleaned, weighed to determine their fresh weight, then chopped and dried in aluminum trays at room temperature for 48 h to allow for water loss. After initial drying, the samples were placed in an oven at 50 °C for 72 h and weighed again to obtain the dry weight. The dried material was then milled and stored. The mineralization of the plant material and the subsequent determination of its mineral content were performed using the same procedures as those applied to the bio-chelates.

2.7. Statistical Analysis

One-way analysis of variance (ANOVA) for statistical differences among treatments was assessed using the Tukey test. The significance level was set at 95% ($p < 0.05$). Statistical analysis was carried out using SPSS 26.0 for Windows (IBM SPSS Inc., New York, NY, USA). Principal component analysis (PCA) was performed for clustering samples and relating them to the different parameters used in the study. This statistical treatment was performed in Origin b9.5.5409 (OriginLab Corporation, Northampton, MA, USA).

3. Results

3.1. Physicochemical Properties of Bioproducts

To quickly elucidate the global distribution of carbon among the main organic groups present in the bioproduct matrices, a solid-state 13C-CPMAS-NMR analysis was conducted. The integrated values for each domain are shown in Table 2.

Table 2. Integration values for the main organic C-type domains in the 13C-CPMAS-NMR spectra of hydrochars with and without activation.

Bioproduct	Chemical Shift Regions (ppm)				
	160–210	**113–160**	**47–113**	**27–47**	**0–27**
	Carbon Distribution (%)				
ASCG	1.52	0.05	84.25	9.10	5.08
AH160	0.08	0.03	83.00	6.15	10.75

Values are shown as % of Total C integration value. ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C.

In the aliphatic carbon region (0–47 ppm), four peaks are highlighted. The first peak, at approximately 11 ppm, indicates the presence of short-chain aliphatic C. The alkyl-N and O C region (47–113 ppm) is the most abundant in all the bioproducts, ranging between 53% and 91%. The peaks at approximately 59, 66, 70, 73, and 78 ppm correspond to alkyl-O C groups from the C-2, C-3, and C-5 atoms in cellulose and hemicellulose. These results confirm that cellulose and hemicellulose are dominant in all bioproducts, but these forms of C decrease as they are transformed by the degradation caused by HTC, more than by activation (Table 2).

The aromatic region (113–160 ppm) and the carboxylic region (160–210 ppm) represent a very low or negligible percentage of the bioproducts' composition (Table 2). It is observed that as hydrothermal carbonization and activation processes are applied, these functional groups completely disappear. The low aromaticity indices exhibited by all bioproducts (ARM, Table 3), align with these findings. However, the total polyphenol content already known in the bioproducts does not appear to be detected by this technique.

Table 3. Structural indices of activated and non-activated bioproducts.

Bioproduct	HB/HI	A/AO	ARM	LR
ASCG	0.2	0.3	0.001	0.2
AH160	0.2	0.1	0.000	0.2

ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C; HB/HI: hydrophobicity; A/AO: alkyl ratio; ARM: aromaticity; LR: lignin ratio.

Regarding the physical properties of the particles, the specific surface area results are shown in Table 4. It is observed that activation of both SCG and hydrochars slightly decreases the specific surface area of the particles, although the values obtained are very low for both activated and non-activated products.

Table 4. BET specific surface area of bioproducts before and after chemical activation.

Bioproduct	Specific Surface (m^2/g)	
	Non-Activated	**Activated**
SCG	0.62 ± 0.01	0.40 ± 0.00
H160	9.15 ± 0.08	6.59 ± 0.04

SCG: spent coffee grounds; H160: hydrochar at 160 °C.

Activation results in products with a neutral pH and a slightly higher EC_{25} (Table 5), which is due to the neutralization with HCl following the NaOH treatment, leading to increased salinity. Differences in salt content among the bioproducts may be subject to operational effects; however, they do not pose a danger for soil application due to the small quantities expected to be used. Regarding the total polyphenol content, activated products have levels ranging from 3.5 to 4.9 mg GAE/g, with ASCG having the lowest content and AH160 having the highest.

Table 5. Physicochemical properties and total phenolic content in activated bioproducts.

Bioproduct	pH	EC_{25} (dS/m)	TP (mg GAE/g)
ASCG	7.4 ± 0.1	2.0 ± 0.1	3.5 ± 0.7
AH160	7.9 ± 0.1	1.6 ± 0.1	4.9 ± 1.1

EC25: electrical conductivity measured at 25 °C. TP: total polyphenols content. GAE: gallic acid equivalents. ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C.

Table 6 shows that the initial Zn content in SCG and hydrochars varies after chemical activation. When SCG and hydrochars are functionalized with Zn salts, the mineral content increases significantly. This effect is amplified when NaOH activation is applied before functionalization. There is also a slight advantage in mineral absorption in hydrochars compared to SCG.

Table 6. Zn content of bioproducts with and without activation and subsequent functionalization.

	Zn (mg/kg)			
Bioproduct	**Non-Ac**	**Ac**	**Non-Ac-Fnc**	**Ac-Fnc**
SCG	10.16 ± 0.44	5.42 ± 0.38	3282.47 ± 35.45	7411 ± 263.09
H160	9.11 ± 1.42	5.83 ± 0.34	859.60 ± 29.90	7376.49 ± 184.70

SCG: spent coffee grounds; H160: hydrochar at 160 °C.

3.2. Total Cumulative Production

The results of the total output per harvest (kg) were divided by 72 m^2 (the area of the plot where the trial was conducted) and summed to represent a cumulative scale. A total cumulative production of 1.92 kg m^{-2} was achieved (Figure 1). The control is the sample that achieved the highest production, reaching 27 kg. Following this are the treatments activated and functionalized with Zn (ASCG-Zn and AH160-Zn). The commercial chelate ranks fourth, which is notable given its common use in greenhouses. Finally, the treatments that increased production the least, especially ASCG, are the activated but non-functionalized bioproducts.

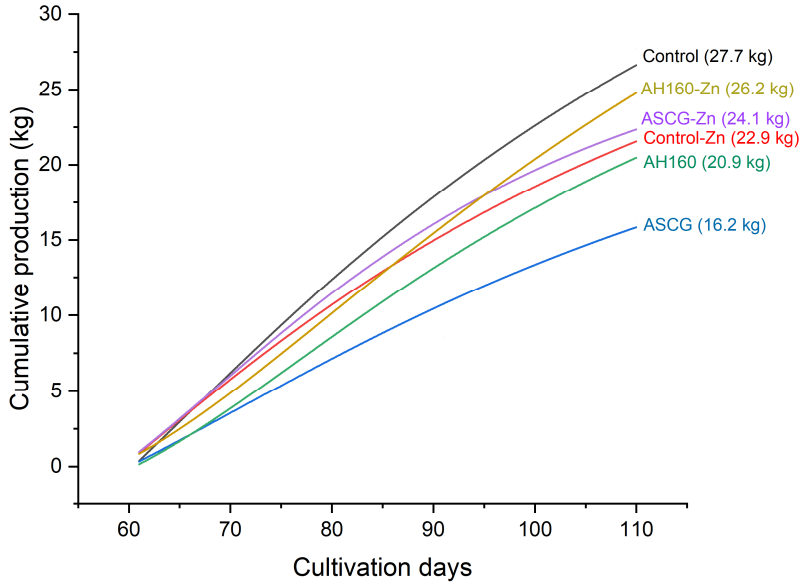

Figure 1. Cumulative production of cucumbers during the trial per treatment. ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C; ASCG-Zn: activated and functionalized spent coffee grounds; AH160-Zn: activated and functionalized hydrochar at 160 °C.

3.3. Zn Content in Cucumbers

Figure 2 shows the distribution of average Zn contents in the three harvests by treatment. The addition of ASCG-Zn and AH160-Zn significantly increased ($p < 0.05$) the Zn content in cucumbers, reaching concentrations of 0.099 and 0.097 mg Zn/100 g fresh weight (FW), respectively. These were followed by the commercial Zn chelate treatment (0.095 mg Zn/100 g FW) and the activated products, both significantly higher ($p < 0.05$) than the control sample (0.085 mg Zn/100 g FW).

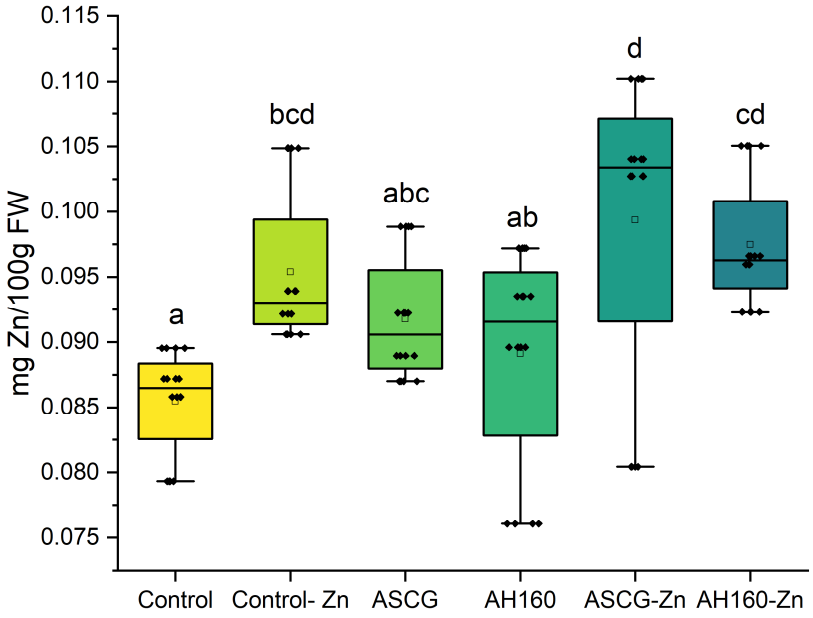

Figure 2. Average Zn content in cucumbers per treatment. ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C; ASCG-Zn: activated and functionalized spent coffee grounds; AH160-Zn: activated and functionalized hydrochar at 160 °C. Different letters indicated statistically significant differences ($p < 0.05$).

The utilization efficiency parameter (Table 7) was calculated for the different treatments. The distribution of this parameter follows this trend: AH160-Zn (0.058) < ASCG-Zn (0.071) < Control-Zn (0.099) < AH160 (13.45) < ASCG (57.22). This result indicates that despite the small amount added by the activated and functionalized bioproducts, cucumbers absorb more Zn than those treated only with functionalized Zn.

Table 7. Utilization efficiency (%) distributed by harvests.

	Utilization Efficiency (%)			
Treatment	**Harvest 1**	**Harvest 2**	**Harvest 3**	**Mean Value**
Control-Zn	0.182	0.074	0.042	0.099
ASCG	73.11	141.88	−43.33	57.22
AH160	41.42	−32.70	31.63	13.45
ASCG-Zn	0.120	0.058	0.036	0.071
AH160-Zn	0.068	0.042	0.064	0.058

ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C; ASCG-Zn: activated and functionalized spent coffee grounds; AH160-Zn: activated and functionalized hydrochar at 160 °C.

Regarding the evolution of Zn in the different harvests, it is observed that the content of this micronutrient increases significantly between the first and second harvest (Figure 3). The greatest increase occurs in the activated SCG, which is also reflected in the utilization efficiency, increasing from 73 to 142. This means that the added Zn remains even more available (either as bio-chelate or naturally contained in the bioproduct, as in the case of the

activated ones) in the second harvest than in the first. However, this pattern is not observed in the third harvest (Figure 3). There is a decrease in Zn content between the second and third harvests in all treatments except for the non-functionalized activated H160, as later observed in the principal component analysis. This is also reflected in the utilization efficiency parameters, where there is an increase from −32.70 to 31.63, the highest value by far in the third harvest.

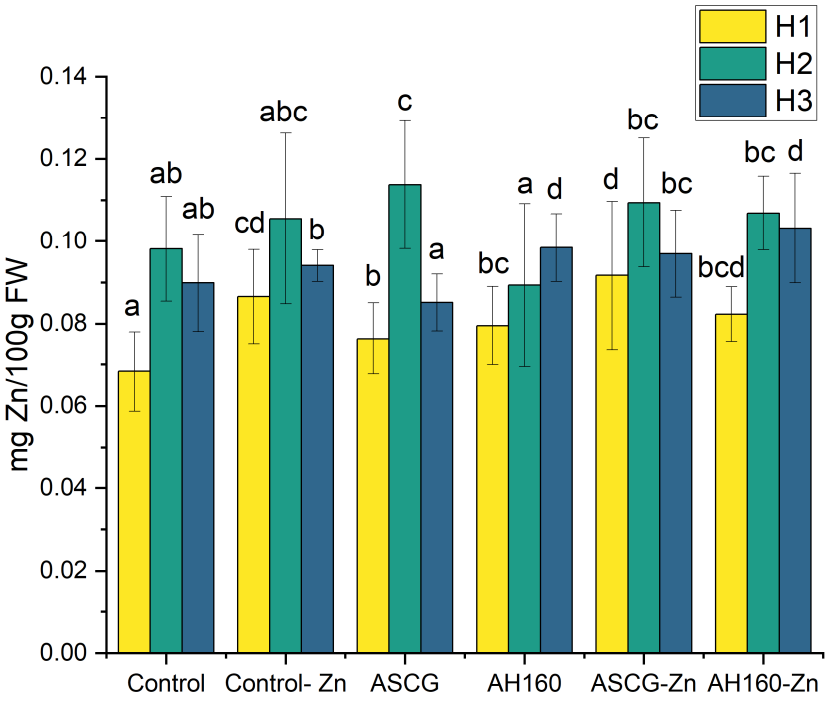

Figure 3. Zn content in cucumbers per treatment, per harvest. Different letters indicated statistically significant differences between different harvests ($p < 0.05$).

4. Discussion

In the review of Pérez-Burillo et al. [24], various applications of SCG and hydrochars were described. Specifically, it was found that both residues can be used as organic amendments to increase soil carbon, as carbon content in Mediterranean soils is below 1% [25]. Additionally, bio-chelates have also been produced with these bioproducts to facilitate the assimilation of these micronutrients by plants and to increase the reserves of Zn and Fe in the soil [9]. It is also important to highlight the environmental benefits of applying coffee grounds and hydrochars. Their application to the soil would help reduce the carbon footprint by reusing a waste product. Additionally, their use as bio-chelates would reduce the need for commercial chelates, which increase soil contamination due to leaching and are also more expensive to obtain.

4.1. Effects of Activation and Functionalization on the Physicochemical Properties of the Tested Bioproducts

The small peak at around 21 ppm is frequently associated in the literature with acetyl groups in hemicellulose [26]. This peak disappears upon activation. The most significant changes in this region are observed in the intensification of the last two peaks at approximately 26 and 30 ppm when the bioproducts are activated. Fuertes et al. [27] attribute these carbons to constituents of liquid polymers. The alkyl-N and O C region (47–113 ppm) are primarily associated with O-substituted alkyl C in carbohydrates, but it also includes methoxyl C and N-substituted alkyl C in proteins [26]. The peaks observed at approximately 100 and 103 ppm represent the anomeric C (C-1) of cellulose [22], which are more prominent in products obtained at HTC temperatures of 160 °C (H160 and AH160). These findings confirm that cellulose and hemicellulose are predominant in all bioproducts.

However, these carbon forms decrease more significantly during the degradation caused by HTC than by activation (Table 2). This decrease, according to Fuertes et al. [27], suggests greater long-term stability of carbons applied to the soil. The higher A/AO values compared to HB/HI (Table 3) corroborate the predominant presence of hydrophilic structures constituting these polysaccharides [27]. The aromatic and carboxylic region completely disappear in the bioproducts' composition. This may be due to the original composition of the raw material or to subsequent decarboxylation processes [27]. Paradowska et al. [28] also did not find visible signals corresponding to phenolic compounds in pollen spectra. The authors attribute their low detection to: (1) insufficient sensitivity established for NMR analysis, and (2) the low concentration of total polyphenols compared to sugars. In the case of SCG by-products, the low detection could be due to the dominant polysaccharide composition of cellulose and hemicellulose, as previously discussed.

Regarding specific surface area, the value obtained for the SCG aligns with what is reported in the literature (0.4 m^2/g) [29]. According to Ballesteros et al. [30], this residue has a low specific surface area due to poorly developed mesopores, a lack of micropores, and a low pore volume (0.004 cm^3/g). On the other hand, contrary to expectations, a decrease in this parameter is observed after activation, as was observed by Zhang et al. [31]. These changes and the pronounced trend toward reducing this parameter may be related to the processes applied to the bioproducts. Both HTC and chemical activation act as degradation processes. Moreover, both processes are carried out in a closed system and aqueous media, which causes degradation material to deposit and adhere to the particles, resulting in activated carbons with obstructed pores and thus a lower contact surface.

Regardless of the specific surface area variation observed, the values obtained both before and after activation are very low compared to other carbons, including those obtained from SCG: 669 m^2/g activated with NaOH [32], 1019 m^2/g activated with $ZnCl_2$ followed by washing [33], and 728 m^2/g activated with H_3PO_4 [34]. The high temperatures applied in those carbonization processes (greater than 450 °C), the type of technique used (pyrolysis), and the subsequent washing applied for the removal of residual degradation material could explain the differences with the specific surface area values obtained for the SCG hydrochars in this study.

The removal of total polyphenols is a significant factor concerning the phytotoxicity of these bioproducts, as noted by some authors [35,36], and therefore could broaden their potential applications in agriculture. One of the strategies to eliminate the phytotoxicity of SCG is their transformation through vermicomposting, thermal hydrolysis, composting, or biochar production. The most effective strategy for the removal of polyphenols (the main cause of phytotoxicity) has been the vermicomposting of SCG [13].

Regarding Zn content in SCG and hydrochars, the results indicate that activation is an effective procedure for enhancing the mineral retention capacity of SCG particles and their hydrochars, despite no improvement in physical properties such as specific surface area, as suggested by Adan-Mas et al. [37]. Hu et al. [38] attribute the improved mineral absorption following NaOH activation to ion exchange, electrostatic attraction, and complexation effects. A study of these mechanisms should be conducted to understand the increased absorption capacity of these activated bioproducts.

4.2. Phytotoxicity Effect

This study found a phytotoxic effect when activated and functionalized bio-chelates were applied to soil compared to the control sample (Figure 1). These results align with the polyphenol content of both bioproducts (Table 5). However, Lara-Ramos et al. [8] did not find such a phytotoxic effect of these same bio-chelates (SCG and hydrochar of 160, 180 and 200 °C) on lettuce plants. However, this kind of bio-inorganic fertilizers did not show this negative effect compared to commercial chelate. Moreover, it could be due to different drawbacks of commercial chelates such as the high solubility of salts and its toxicity for plants [6,39]. The same does not apply to bio-chelates that are only functionalized and not activated. The study of Lara-Ramos et al. [8] revealed that applying these bio-chelates

reduced phytotoxicity in lettuce and boosted the zinc content in plants by 318.2% when hydrochar activated and functionalized with zinc at 180 °C was used. In the case of SCG, it does not lead to the cumulative production of 15 kg. It has been known for years that the application of SCG [36] and hydrochar derived from SCG [34] generates a phytotoxic effect in lettuce plants when they are grown in bioclimatic chambers. This phytotoxicity has been primarily attributed to the polyphenol content of the SCG and the higher content of these compounds when SCG are subjected to hydrothermal carbonization [13]. To this end, strategies have been studied to eliminate the polyphenol content of SCG. The most promising approach has been vermicomposting of these residues, followed by biochar production [13].

4.3. Zn Content in Cucumber Plants

The addition of ASCG-Zn significatively increased ($p < 0.05$) the content of Zn in cucumber plants until 0.099 mg Zn/100 g fresh weight (FW) compared to control sample and when AH160-Zn was applied until 0.097 mg Zn/100 g FW. In the case of Lara-Ramos et al. [8], both SCG and hydrochars promoted similar Zn levels in plant (0.30–0.35 mg Zn 100 g^{-1} fresh weight. These amounts are lower compared to cucumber crops as they apply to lettuce cultivation. This difference may be due to the cultivation period: in the case of lettuce, there is only one harvest with a duration of 45 days, whereas for cucumber, there are three harvests with a cultivation period of 110 days. Commercial chelate (control-Zn) also has a biofortifying effect, like ASCG-Zn. This confirms chelates as one of the most efficient tools to increase micronutrients in crops [40].

Concerning the different harvests (Figure 3), an increase in Zn content between the first and second harvests can be observed in all cases. This is a very important result, as it suggests an increase in the Zn reserve in the soil, leading to positive utilization efficiency except in the case of AH160, where a smaller increase is observed compared to the other treatments. However, in almost all cases (except for AH160), there is a leaching of Zn in the third harvest, and it does not seem to be bioavailable for cucumbers. This may be due to the continuous leaching of elements, which occurs as a result of constant irrigation since the irrigation water contains many salts. Only in the case of AH160 is the Zn reserve in the soil maintained even in the third harvest, which may be because AH160 degrades more slowly as a result of the hydrothermal carbonization process. In this case, the application of H160 would leave a reserve of Zn in the soil.

4.4. Principal Component Analysis (PCA)

A principal component analysis was performed to analyze the comprehensive response of the Zn content in cucumbers to the addition of bioproducts activated and functionalized (Figure 4). A matrix contained the values of content of Zn in harvest 1 (Zn_H1), harvest 2 (Zn_H2), and harvest 3 (Zn_H3), and the average of the three harvests (Zn_average) was selected. Figure 4 shows the space defined by PC1 and PC2 (which capture 85.85% of variance) with the score values of the samples. The first component explained the 57.13% of the variance and group samples according to their effect on Zn content in cucumbers. The higher values on PC1 correspond to ASCG-Zn and AH160-Zn, with higher contents of Zn in cucumbers. PC2, explaining the 28.72% of the variance group samples according to the distribution of Zn content in the different harvests. Positive values correspond to samples with higher Zn content in the third and first harvest and negative values correspond to Zn-average and second harvest. The positive values are close to AH160, and the negative values are close to ASCG. The positive values in AH160 are due to it being the only treatment that significantly increases Zn content in the third harvest. PCA analysis confirms what has been previously highlighted regarding Zn content in cucumbers.

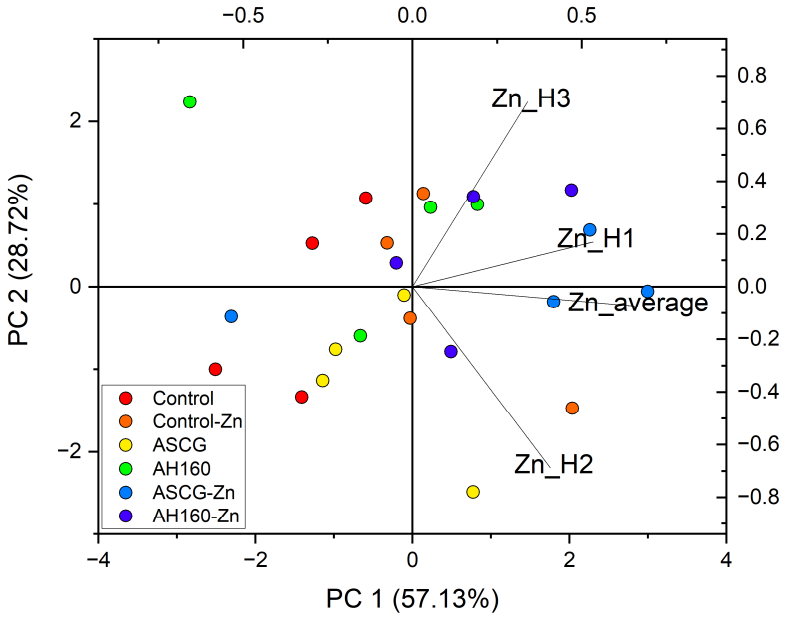

Figure 4. Superimposed graph of PCA scores obtained for samples (PC2 vs. PC1) and loadings. ASCG: activated spent coffee grounds; AH160: activated hydrochar at 160 °C; ASCG-Zn: activated and functionalized spent coffee grounds; AH160-Zn: activated and functionalized hydrochar at 160 °C; Zn_H1: Zn harvest 1; Zn_H2: Zn harvest 2; Zn_H3: Zn harvest 3.

5. Conclusions

Activation and functionalization are relatively straightforward procedures that significantly enhance the performance of these bioproducts as biofortifying agents. The activation of both SCG and hydrochar at 160 °C decreases the specific surface area of the particles. When these by-products were functionalized, the Zn content increases significantly. Regarding the cumulative production, the by-products activated and functionalized with Zn were the samples that achieved the highest production. Adding these by-products significantly increases the Zn content in cucumbers, reaching concentrations of approximately 0.1 mg Zn/100 g fresh weight. Activated by-products achieved the highest utilization efficiency. This improvement is based on a net increase in Zn content in the bioproducts compared to those that are neither activated nor functionalized. Addressing the Zn content results in cucumbers (either as an average or as a sequential content across all harvests) presents a dilemma regarding the selection of the optimal bioproduct. On one hand, SCG, with fewer transformations, results in a more biofortified cucumber. On the other hand, Zn content appears to be maintained across harvests when hydrochar is added. An economic and functional study would be necessary to determine which bioproduct is the best choice. This is particularly interesting since these greenhouses use a continuous excess of water (which leads to leaching) to prevent salinity. Additionally, hydrothermal carbonization is part of the circular economy and produces other liquid by-products that have not been considered in this case, highlighting the need for a comprehensive evaluation. Regarding commercial Zn chelates, they exhibit a stronger biofortifying effect and slightly lower toxicity compared to the commercial chelates.

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