



Advanced Characterization of Biochars Produced from Three Different Organic-based Feedstocks and their Potential Applications

Anna Kritikaki¹ · Vasiliki Karmali¹ · Dimitra Vathi¹ · Georgios Bartzas¹ · Konstantinos Komnitsas¹

Received: 25 November 2024 / Accepted: 15 April 2025 / Published online: 24 April 2025
© The Author(s) 2025

Abstract

The present paper discusses the properties of biochars produced from different feedstocks, namely sewage sludge (SS), olive tree pruning (OTP) and walnut shells (WS), after slow pyrolysis at 300–400 °C. The techniques used for their characterization are X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TG) and Scanning Electron Microscopy (SEM). In addition, the toxicity of the feedstocks and the produced biochars was assessed with the use of EN 12457-2 test. Furthermore, the phytotoxicity of substrates, containing test soil, 20 wt% biochar and / or 190 mg/kg Cu was evaluated for three seeds, namely *Lepidium sativum* (LS), *Sinapis alba* (SA) and *Sorghum saccharatum* (SC), with the use of Phytotoxkit microbiotest kit (MicroBioTests Inc., Belgium) and the determination of the germination index (GI). The experimental results clearly show that both the feedstock type and the pyrolysis temperature affect the physicochemical properties of the produced biochars. The pyrolysis yield decreases with the increase of pyrolysis temperature and may reach values as low as 10% for OTP biochar. According to the International Biochar Initiative (IBI) sewage sludge biochar is classified as Class III because its C_{org} content varies between 10% and 30%, while OTP and WS biochars belong to Class I as their C_{org} content is well above 60%. The application of EN 12457-2 test indicates that the produced biochars exhibit no toxicity. Finally, the addition of biochar in substrates has either phytostimulant or phytotoxic effect depending on the type of the seed used and the contamination with Cu ions.

Keywords Olive tree pruning · Walnut shells · Sewage sludge · Germination index · Biochar phytotoxicity, microstructure

Abbreviations

AC Ash content

✉ Konstantinos Komnitsas
kkomnitsas@tuc.gr

¹ School of Mineral Resources Engineering, Technical University of Crete, Chania 73100, Greece

BSI	Backscattered electron images
C _{org}	Organic carbon
EBC	European Biochar Certificate
EC	Electrical conductivity
FTIR	Fourier transform infrared spectroscopy
GHG	Greenhouse gas
GI	Germination index
IBI	International Biochar Initiative
LS	Lepidium sativum
OTP	Olive tree pruning
SA	Sinapis alba
SC	Sorghum saccharatum
SS	Sewage sludge
SEM	Scanning Electron Microscopy
TG	Thermogravimetric analysis
TS	Total solids
VM	volatile matter
WS	Walnut shells
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
y _p	Pyrolysis yield

Introduction

Biochar is a carbon-rich material with a fine-grained and porous structure, that is produced after pyrolysis of biomass (i.e. wood, agricultural and food wastes, sewage sludge, etc.) at low to average temperature (250–700 °C) in an inert atmosphere [1]. It has significant chemical and physical properties; thus, it may be suitable for several agricultural applications [2, 3]. Due to its varying carbon and nutrients content it can be used as soil supplement to enhance nutrient availability in plants and improve crop growth [4]. In addition, the hydrophobic nature of most biochars and the presence of both aliphatic and aromatic compounds result in increased C stability in soils [5–7]. Biochars with an O/C_{org} ratio less than 0.2 have very high stability and their half-life may exceed 1000 years [8]. Thus, biochar addition on soils may prove as an effective climate change mitigation practice and prevent to a certain degree global warming [9, 10].

Biochar can also act as slow-release fertilizer and improve soil properties, i.e. water retention capacity, moisture and nutrient content [11, 12]. Due to its porous structure, high specific surface area, cation exchange capacity and adsorption potential, it can be successfully used as soil amendments, as well as for the adsorption of contaminants, including heavy metals and metalloids, and the remediation of contaminated soils [13]. It is mentioned that the porosity and the surface area of biochars can be substantially increased after modification with several chemical agents [14].

So far, various types of feedstocks have been tested for the production of biochar. One of them is sewage sludge (SS) that is produced in huge quantities in wastewater treatment plants and in several cases is not managed properly and causes environmental problems [15,

16]. Zong et al. [17] discussed in detail the production of SS biochar after thermal treatment and its application on soils. In addition, the biochar produced from SS can be also used in several environmental applications as catalyst and support material in advanced oxidation processes, or as adsorbent for the removal of contaminants from waters, wastewaters and soils [18]. On the other hand, only a relatively small number of studies investigate its use in agriculture. Racek et al. [19], studied the effect of pyrolysis conditions on the physical and chemical properties of SS biochar and its potential application in agriculture. In another review paper the use of SS biochar to remediate soils, reduce CO₂ emissions, and remove contaminants from waters is highlighted [20]. He et al. [21], state that biochar addition has a positive effect on several chemical, biological and physical properties of soils, including pH, nutrient retention capacity and C stability. SS biochar can also enhance soil health and crop productivity; it is reported that soils amended with 2 wt% biochar results in higher biomass yield of winter wheat and spinach crops and in improved soil aggregates stability [22]. Lilli et al. [23], mention that SS biochar addition in field tests during tomato cultivation resulted in improved soil characteristics, higher C and P sequestration and higher yield. Zong et al. [17] also observed that the addition of SS biochar on two different ultisols buffered soil acidity and improved its physical properties.

Another source of agricultural waste that is produced in significant quantities in many Mediterranean countries and can be used for the production of biochar is olive tree pruning (OTP); it is known that burning, which is a common OTP management practice, results in increased greenhouse gas (GHG) emissions [24]. On the other hand, biochar derived from OTP may be used as soil amendment to improve plant growth and carbon stability [25] as well as to adsorb contaminants from soils [26–28].

Walnut shells (WS) is another type of agriculture waste that is abundant in several countries and can be utilized for biochar production. Most studies dealing with the valorisation of walnut shells focus on their use in cosmetics and pharmaceutical applications [29–31], while some other explore their use as absorbents for the removal of harmful compounds from wastewaters [32–34]. So far, only a few studies investigated the production of biochar from walnut shells and its addition in soils to improve seed germination and early growth of seedlings of fodder crops [35–37].

Overall, most studies concerning the application of biochar in agriculture focus on its use as soil amendment as well as for C sequestration, uptake of contaminants and phytotoxicity reduction. It is known that high content of certain contaminants in soil hinders water and nutrients uptake, induces oxidative stress and disrupts photosynthesis, resulting in reduced biomass production and yield [38–40].

The present study characterizes in detail three different biochars, two of which are produced from the pyrolysis of agricultural wastes and one from sewage sludge, a municipal waste that is produced in large quantities in almost every city. In addition, the study focuses on (i) the identification of biochar microstructure with the use of analytical techniques, (ii) the assessment of its toxicity with the use of EN 12457 -2 test, and (iii) the effect of biochar addition on the phytotoxicity of three seeds, namely *Lepidium sativum* (LS, garden cress), *Sinapis alba* (SA, mustard) and *Sorghum saccharatum* (SC, Sorgho), in substrates contaminated with Cu ions.

Materials and Methods

For the production of biochar three different feedstocks namely (i) sewage sludge (SS) provided by the Wastewater Treatment Plant (WWTP) of Chania, Crete, Greece, (ii) olive tree pruning (OTP) obtained from a local farm in Chania and (iii) walnut shells (WS) obtained from a farm in Lamia, central Greece, were subjected to slow pyrolysis. All biomasses were initially oven-dried (Carbolite, Germany) at 105 °C for 24 h. The pyrolysis of the biomasses was carried out in a laboratory furnace (LHT08/17 Nabertherm), at three different temperatures i.e. 300 °C, 350 °C and 400 °C. In order to maintain an inert atmosphere, nitrogen was fed in the furnace at a rate of 100 mL/min. The heating rate was maintained at 10 °C min⁻¹ and the retention time of the feedstock in each of the selected temperature was 60 min.

Proximate analysis of biomasses and the produced biochars was performed using the following standards; total solids (TS), APHA–AWWA–WEF 2540 B; moisture, ASTM D2216–19; volatile solids (dry basis) (VS), APHA–AWWA–WEF 2540 G; and ash content (AC) (dry basis), ASTM E1755–01. Pyrolysis yield (y_p) was determined for all biochars from the % weight loss of the associated feedstocks.

XRD analysis was performed using an X-ray diffractometer (Bruker AXS, D8–Advance, Bruker, Karlsruhe, Germany) with a Cu tube, LynxEye detector with Ni filter and scanning range from 0 to 70° 2 Theta (2 θ), step size of 0.02°, and 0.4 s/step measuring time. Mineralogical phases were identified with the DiffracPlus Software (EVA v. 4.2, Bruker, Karlsruhe, Germany) and the Crystallographic Open Database (COD database), while for the quantitative determination of mineralogical phases the Rietveld software AutoQuan v.2.8 (Seifert GE) was used.

Chemical analysis of biochars for the determination of inorganic compounds was carried out using an X-Ray fluorescence energy dispersive spectrometer (XRF-EDS) Bruker-AXS S2 Range Type. Elemental analysis C, H, S and N analysis was performed according to ASTM 5373 standard in a flash 2000 elemental analyzer thermo scientific calibrated using 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT) standards. Inorganic C was determined by the addition of 1 N HCl as described in ASTM D4373 standard. Organic C (C_{org}) was determined by deducting the content of inorganic carbon from the content of total carbon. pH and electric conductivity (EC), (EPA Method 9045D, ASTM D4972 - 19) were measured using a solid to liquid (L/S) ratio of 1/10 (w/v) and a Hanna 211 pH/Eh meter and bench conductivity EC215 meter, respectively.

Thermogravimetric analysis (TG) was performed after heating all feedstocks to 850 °C to determine the percentage weight loss and estimate the volatile matter (VM) and char content (%). The test was conducted using the TGA- 6/DTG analyzer (Perkin Elmer) with a temperature accuracy of ± 2 °C and a balance sensitivity of < 5 μ g.

Fourier-transform infrared (FTIR) spectroscopy analysis was carried out to identify the functional groups present in biomass and the produced biochars using KBr pellets; each sample was mixed with KBr at a ratio 1:100 w/w in a Perkin Elmer Spectrum 1000 Spectrometer.

The microstructure of the samples was determined by Scanning Electron Microscopy (SEM) using a JEOL 6380LV scanning electron microscope equipped with an EDS INCA microanalysis system.

EN 12457 -2 (L/S =10 L/kg) [41] compliance test was performed in all samples to determine leaching of potentially hazardous elements (PHEs). The concentration of Cr, Ni, Zn, Cd, Pb and Cu in the extract was determined using an Agilent Technologies 7500c x inductively coupled plasma mass spectrometry (ICP-MS) analyzer (Agilent Technologies, Santa Clara, CA, USA).

Finally, the phytotoxicity of the substrates was evaluated using the Phytotoxkit micro-biotest (MicroBioTests Inc., Belgium) test that uses a control reference soil as indicated by the Organisation for Economic Co-operation and Development (OECD). The treatments investigated were:

- i) test soil (garden soil).
- ii) test soil and addition of 20 wt% (200 g/kg) of SS, WS and OTP biochar; each biochar was added separately.
- iii) test soil contaminated with 190 mg/kg Cu.
- iv) test soil contaminated with 190 mg/kg Cu and addition of 20 wt% of SS, WS and OTP biochars.

The soil was contaminated with 190 mg/kg Cu because this is the Intervention Value proposed in the Dutch standards for soils and sediments [42].

20 g of the above-mentioned substrates, moistened with a specific amount of deionized water that corresponds to soil water holding capacity, were transferred in a container with a lid. A filter paper was placed on the top of the hydrated soil - biochar layer. Ten seeds of LS, SA and SC were placed on the filter paper in equal spacing. The number of germinated seeds and their mean root length was evaluated after 3 days of incubation. The germination index (GI), an indicator of biochar toxicity, was calculated using the following Eqs. [43, 44]:

$$GI = \frac{g_t l_t}{g_c l_c} 100\%$$

where,

g_t : number of germinated seeds in test soil (%), l_t : average root length in test soil, in mm, g_c : number of germinated seeds in control soil (%), and l_c average root length in control soil, in mm.

All tests were carried out in triplicate.

Results and Discussion

Physico-chemical Properties

The chemical analysis of biochars, produced after slow pyrolysis at 400 °C, in the form of oxides, is shown in Table 1.

It is observed from this data that the SS biochar has high content of CaO (17.8%), P₂O₅ (17.5%), Na₂O (11.9%), SiO₂ (10.5%), and Fe₂O₃ (10.1%). These results are in general terms similar to those derived from earlier studies; however, minor differences may occur due to the quality of the sewage sludge that depends on the treatment methods used in dif-

Table 1 Chemical analyses (wt.%) of the produced biochars at 400 °C

	SS	OTP	WS
Na ₂ O	11.9	2.6	0.9
MgO	5.6	1.3	0.3
Al ₂ O ₃	3.3	0.2	0.03
SiO ₂	10.5	1.1	0.1
P ₂ O ₅	17.5	2.0	0.5
SO ₃	3.8	0.9	0.1
K ₂ O	0.8	5.5	1.8
CaO	17.8	9.8	1.9
TiO ₂	0.8	0.03	0.003
Cr ₂ O ₃	0.021	0.004	0.001
MnO	0.1	0.01	0.003
Fe ₂ O ₃	10.1	0.2	0.04
CoO	n.d*	0.001	0.01
NiO	0.01	0.01	0.001
CuO	0.1	0.004	0.002
ZnO	0.3	0.01	0.002
As	0.001	n.d	n.d
Se	0.0007	0.0001	n.d

n.d not detected

ferent wastewater treatment plants [45–48]. On the other hand, both OTP and WS biochars have lower CaO and K₂O content, namely 9.8% and 5.5% for OTP, and 1.9% and 1.8% for WS, respectively. The chemical analyses of the biochars produced at 300 and 350 °C (not shown) are quite similar with those presented in Table 1.

Selected physico-chemical properties of feedstocks and the produced biochars are shown in Table 2. It is seen that all feedstocks exhibit pH values higher than 8 which increase slightly in the biochars produced at higher pyrolysis temperature, due to the decomposition of functional groups and the formation of carbonates. The high pH value (8.5) of SS feedstock is due to the addition of lime, a common practice followed in wastewater treatment plants (WWTPs) to eliminate pathogens and odors. Thus, biochars with higher pH may be applied in acidic soils to buffer pH and improve seed germination [35, 49]. Also, as shown in other studies, alkaline amendments may be used for the reduction of aluminum toxicity in acidic soils [50, 51], or for the adsorption of negatively charged ions [52, 53].

Electrical conductivity (EC) is a key parameter that denotes the amount of total dissolved salts in feedstocks and biochars and thus affects soil characteristics and the leachability of hazardous elements. The EC in all feedstocks and the produced biochars has low values ranging from 0.7 to 2.4 mS cm⁻¹ and 0.3 to 1.7 mS cm⁻¹, respectively, as also mentioned in earlier studies [25, 54].

The specific surface area (SSA) of all feedstocks is low; on the other hand, the SSA of the produced biochars increases with pyrolysis temperature and reaches higher values, ranging between 25 and 45 m² g⁻¹ at 400 °C. SSA indicates the potential of biochars to act as adsorbents, slow-release fertilisers or soil conditioners. It is known that further increase in the SSA, if required for a specific application, can be achieved through chemical activation [55, 56]. However, this step increases production cost and may have adverse impacts after the application of biochar in soils.

Furthermore, pyrolysis yield decreases with increased pyrolysis temperature; this is more clearly seen in the OTP biochar that has a very low yield at 400 °C, only 10%. The decrease

Table 2 Selected properties of SS, OTP and WS feedstocks and the produced biochars at 300, 350 and 400°C

Parameter	SS				OTP				WS			
	Initial	300	350	400	Initial	300	350	400	Initial	300	350	400
pH	8.5	8.7	8.9	10.1	8.4	8.9	9.1	9.2	8.3	8.6	8.9	9
EC, mS cm ⁻¹	2.4	1.7	1.6	1.5	1.0	0.8	0.7	0.6	0.7	0.4	0.3	0.3
SSA*, m ² g ⁻¹	1.2	7.6	12.8	45.7	7.8	15.3	23.7	30.5	2.1	11.2	19.6	24.7
Yield, %	-	30	27	25	-	24	15	10	-	41	35	23
Moisture, %	69.2	8	7	3.5	18.3	13.1	2.4	1.1	11.4	7	4	1
Ash, %	25	29	34	47	3.5	4.7	8.6	14.7	2.8	5.8	10.7	22.3

*SSA specific surface area

in yield is the result of the condensation of aliphatic compounds and the generation of CH_4 , H_2 and CO during pyrolysis. Dehydration of hydroxyl groups and thermal degradation of lignocellulose structures occurs at higher temperature range (500–700 °C) and can result in even lower yield [57].

Moisture content is a crucial parameter that influences the yield of the biochar for a given pyrolysis time. As the temperature increases, the moisture content of all biochars decreases and may become as low as 1% after pyrolysis at 400 °C.

Finally, sewage sludge biochar contains a higher percentage of ash (max. 47%), followed by the WS (max. 22%) and OTP (max. 15%). The increase of pyrolysis temperature results in increased ash content for all biochars. This is mainly, at least for SS, due to its high mineral content that is accumulated into the ash after pyrolysis at higher temperature [18], as well as the decomposition of volatile compounds [58].

The elemental analysis of biomasses and the produced biochars is presented in Table 3.

It is seen that the content of C, H, N, S and O varies widely among feedstocks and the produced biochars. A low content of S (1.8 wt%) is only present in the as-received sample of SS.

As anticipated, sewage sludge, obtained from the local wastewater treatment plant, has higher content of nutrients. The content of nutrients in biochars determine their agricultural application potential, that also depends on the availability of nutrients in soils and the respective needs of cultivated species.

The C content in the SS biochar decreases from 31 to 12 wt% with the increase of the pyrolysis temperature to 400 °C, as also mentioned in other studies [59]. This decrease is associated with the volatilization of the C species and also depends on the wastewater treatment process and the quality of the sewage sludge [60, 61]. On the other hand, the carbon content of OTP and WS biochars increases with the increase of the pyrolysis temperature and varies between 75 and 80% at 400°C.

Sewage sludge biochar, with a C_{org} content exceeding 10% is classified as Class III [1, 8]. On the other hand, OTP and WS biochars belong to Class I, as their C_{org} content is much higher than 60%.

Furthermore, it is mentioned that the $\text{H}/\text{C}_{\text{org}}$ molar ratio is an indicator of carbon stability. Values of $\text{H}/\text{C}_{\text{org}}$ lower than 0.7 indicate that the biochar has not been thermochemically altered. All biochars produced in this study have very low $\text{H}/\text{C}_{\text{org}}$ ratios, due to the presence of resistant to decomposition aromatic ring structures, and thus they are characterised by high carbon stability [58].

On the other hand, the $\text{O}/\text{C}_{\text{org}}$ ratio varies broadly in the produced biochars; in the SS biochar it varies between 5 and 10, while in the OTP and WS biochars between 0.2 and 0.4 and 0.3–0.7, respectively. Lower $\text{O}/\text{C}_{\text{org}}$ ratios indicate longer biochar half-lives and higher potential for C sequestration [8]. When this ratio is higher than 0.6 biochars may have half-life smaller than 100 years, while ratios ranging from 0.2 to 0.6 indicate a half-life between 100 and 1000 years, and ratios lower than 0.2 indicate a half-life exceeding 1000 years [62].

Finally, the C/N ratios vary widely among the feedstocks and the produced biochars. High C/N ratios, as observed in both OTP and WS biochars, indicate noticeable content of recalcitrant C. As mentioned in other studies, the application of biochar with a high C/N ratio on soil, may result in immobilisation of nitrogen by microbes and increased number of carbon species [63, 64].

Parameter	SS				OTP				WS			
	Initial	300	350	400	Initial	300	350	400	Initial	300	350	400
C (wt.%)	30.8	26.5	16	12.2	26.9	65.4	70	80.6	50.4	53.9	74.3	75.1
H (wt.%)	4.9	1.6.8	1.0	0.7	0.3	1.3	1.1	0.8	0.4	1.3	1.1	0.5
N (wt.%)	6.0	3.1	3.3	4.8	2.9	3.8	5	3.4	6.8	4	2.4	2.9
S (wt.%)	1.8	-	-	-	-	-	-	-	-	-	-	-
O (wt.%)	56.5	69.3	80.7	82.2	52.8	29.5	23.9	14.6	42.4	51.79	22	21.5
C _{org} (wt.%)	6.4	12.3	16.4	19.7	52.1	71.3	72.7	76.5	66.2	81.2	82.5	83.7
H/C _{org}	0.76	0.13	0.06	0.04	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
O/C _{org}	8.8	5.6	4.9	4.2	1.0	0.4	0.3	0.2	0.6	0.7	0.3	0.3
C/N	5.1	8.6	7.0	2.5	15.2	17.2	14.0	23.7	7.4	11.9	31.0	26.0

Mineralogical Analysis -morphology

Figure 1 shows the XRD patterns of SS feedstock and the produced biochars. The feedstock has several crystalline phases, including quartz (Q), calcium compounds namely calcite (CaCO_3), larnite (Ca_2SiO_4), and hedenbergite ($\text{CaFe}_2\text{Si}_2\text{O}_6$), as well as hematite (Fe_2O_3) and halite (NaCl) (Fig. 1a); the intensity of these peaks changes after pyrolysis at higher temperature (Fig. 1b and d). It is also seen that the feedstock has a peak of cellulose that is modified in the produced biochars as a result of partial decomposition of organic compounds [65].

The XRD patterns of OTP feedstock and the produced biochars are shown in Fig. 2. The peak seen at 22° 2-theta is attributed to cellulose (C) (Fig. 2a) and is shifted slightly after pyrolysis, as also mentioned in other studies [28]. When pyrolysis takes place at above 350°C cellulose, hemicellulose and lignin present in the feedstocks are partially decomposed (Fig. 2b and d) [66]. At higher pyrolysis temperature crystalline phases, such as magnesium calcite (MC) ($\text{Ca}_{0.94}\text{Mg}_{0.06}\text{CO}_3$) and halite (H) are detected (Fig. 2d).

Figure 3 shows the XRD patterns of WS feedstock and the produced biochars. It is seen that cellulose is the main phase shown in the feedstock whereas no other phases are identified in the produced biochars in sufficient quantities.

Figure 4 shows the FTIR spectra of SS feedstock and the produced biochars. The spectrum of SS (Fig. 4a) has several intense peaks, while fewer and smaller peaks are observed in the produced biochars (Fig. 4b–d). The peaks at 2930 cm^{-1} , 2840 cm^{-1} and 1576 cm^{-1} in SS are associated with organic compounds, while the peaks at 1650 cm^{-1} , 1440 cm^{-1} , and 888 cm^{-1} are attributed to calcium compounds [67, 68]. The peak intensity at 1650 cm^{-1} and 1440 cm^{-1} in the produced biochars is reduced. The peaks at 1140 cm^{-1} and 456 cm^{-1} are attributed to either stretching vibrations of the C–O bond or the presence of inorganic compounds [69].

In OTP spectra (Fig. 5), the initial peak at 3400 cm^{-1} , which is more clearly shown in the feedstock, corresponds to hydroxyl bonds (–OH). The peaks at 2910 cm^{-1} and 2858 cm^{-1} are associated with symmetric and asymmetric stretching vibrations, respectively, of the CH_2 bonds of cellulose, hemicellulose, and lignin. As the pyrolysis temperature increases, these bonds become less intense. The small peak shown only in the feedstock at 2364 cm^{-1} corresponds to a triple bond of nitrile or alkynes [6]. The peaks at 1578 cm^{-1} shown in feedstock and at 1633 cm^{-1} in biochars are due to vibrations of the stretching mode of the C=O bonds. The absorption band at 1378 cm^{-1} is attributed to vibrations of the C=H bond in alkane and alkyl groups. The absorption band at 888 cm^{-1} is associated with out-of-plane bending vibrations of the C–H bond [48], while the absorption bands at 1428 cm^{-1} and 492 cm^{-1} are assigned to carbonates and inorganic compounds, respectively.

The FTIR spectrum of the WS feedstock (Fig. 6a) show the presence of peaks at 2910 cm^{-1} and 2858 cm^{-1} as in Fig. 5a, with much lower intensity though. The peaks observed near 1600 cm^{-1} and 1700 cm^{-1} in biochars (Fig. 6b–d) are mainly due to the stretching vibrations of the (C=C) bonds in aromatic compounds and alkenes. Similarly, the peak at 1380 cm^{-1} , more clearly shown in OTP biochars, corresponds to vibrations of the C=H bond, while the peak at 1220 cm^{-1} is attributed to stretching vibrations of the C–O bond. Finally, the peaks at 888 cm^{-1} and 550 cm^{-1} , which are more intense at higher pyrolysis temperatures, are attributed to the presence of inorganic compounds [70].

Figure 7 presents the thermogravimetric (TG) analysis of the feedstocks. The weight loss of about 10% at 100°C is associated with the removal of moisture, while the weight

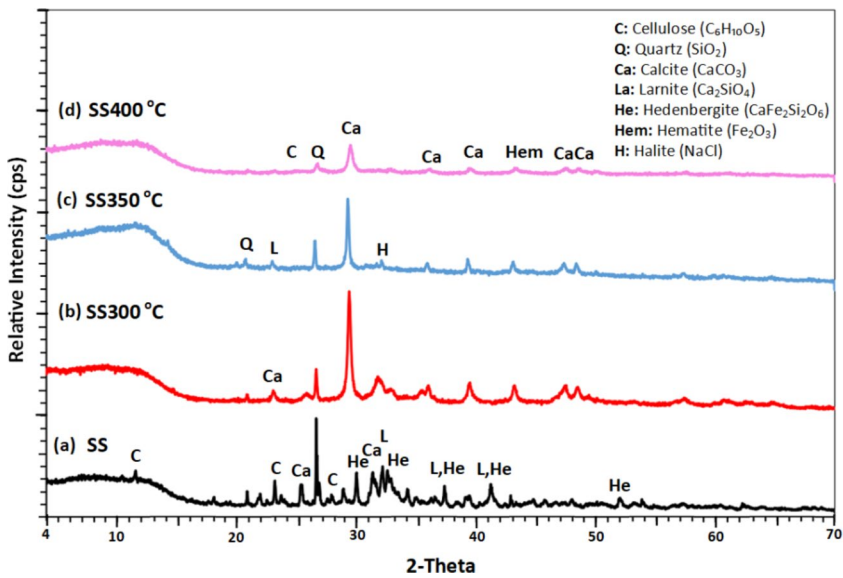


Fig. 1 XRD patterns of (a) sewage sludge feedstock (a) and the produced biochars (b) SS 300 °C, (c) SS 350 °C and (d) SS400 °C (C: cellulose, Ca: Calcite, Q: Quartz, L: Larnite, H: Halite, He: Hedenbergite, Hem: Hematite)

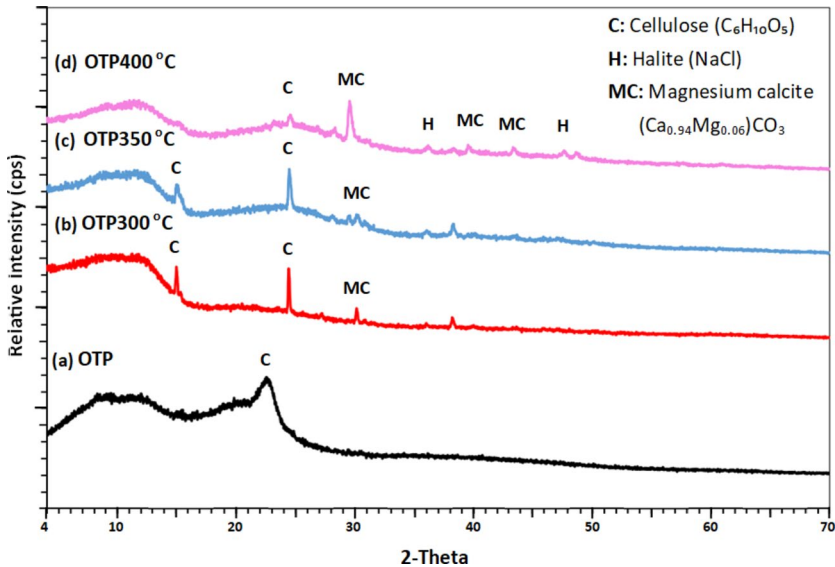


Fig. 2 XRD patterns of (a) OTP sludge feedstock and the produced biochars (b) OTP300 °C, (c) OTP350 °C and (d) OTP400 °C (C: cellulose H: halite. MC: Magnesium calcite)

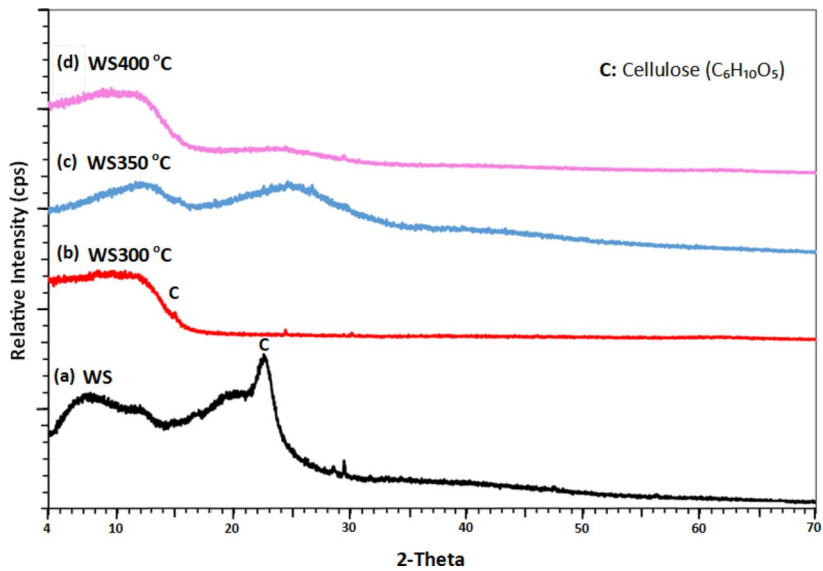


Fig. 3 XRD patterns of (a) walnut shell feedstock (WS) and the produced biochars (b) WS300 °C, (c) WS 350 °C and WS400 °C (d) (C: cellulose)

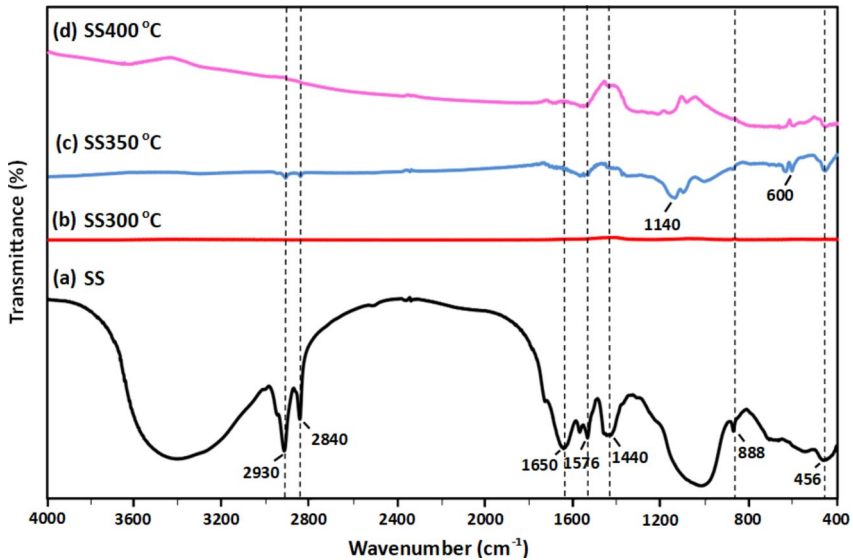


Fig. 4 FTIR spectra of (a) sewage sludge feedstock and the produced biochars (b) SS 300, (c) SS 350, and (d) SS 400 °C

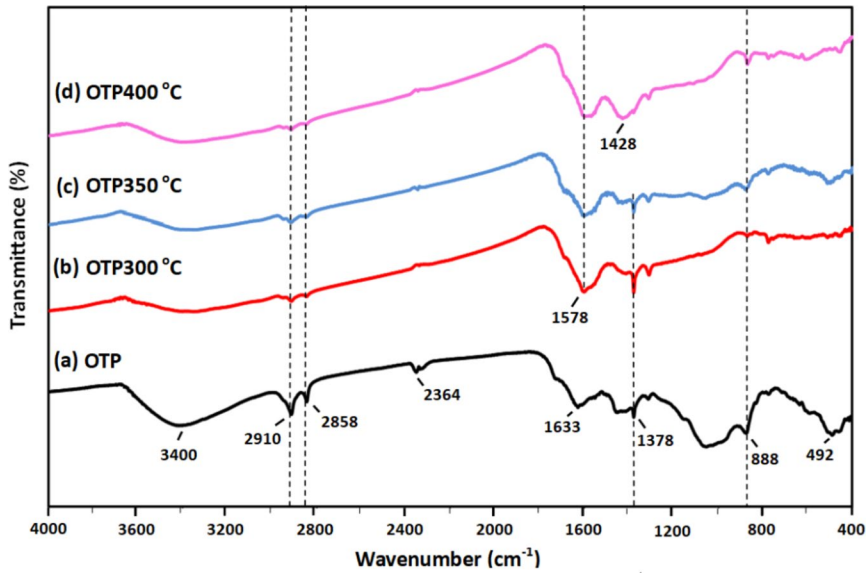


Fig. 5 FTIR spectra of (a) OTP feedstock and the produced biochars (b) SS 300, (c) SS 350, and (d) SS 400 °C

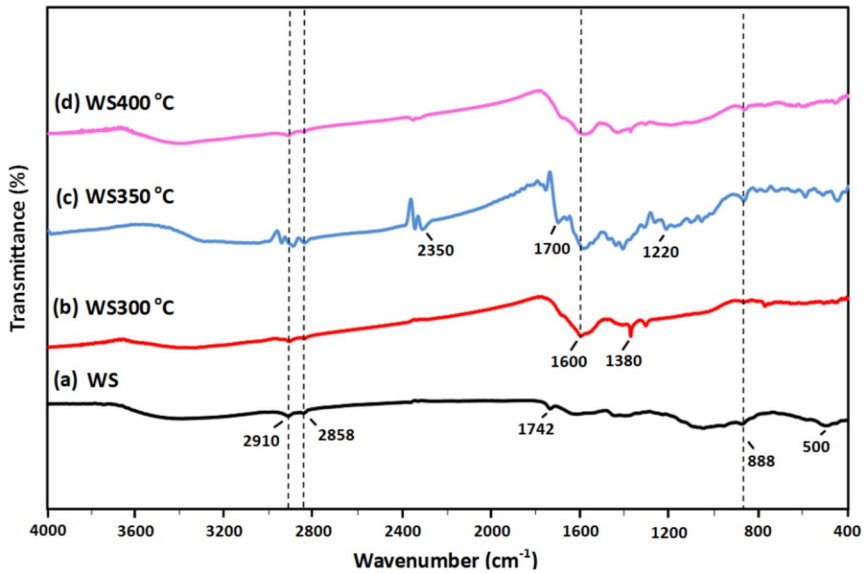


Fig. 6 FTIR spectra of (a) WS feedstock and the produced biochars (b) WS 300, (c) WS 350, and (d) WS 400 °C

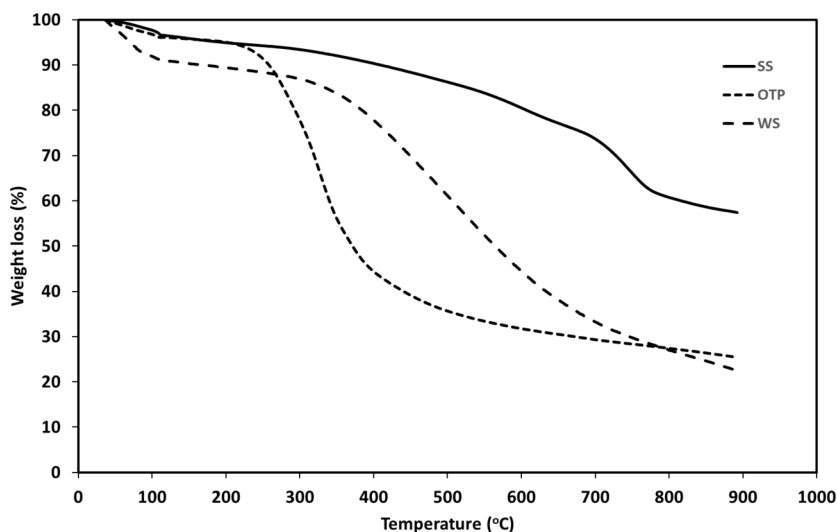


Fig. 7 Thermogravimetric (TG) analysis of sewage sludge (SS), olive tree pruning (OTP), and walnut shells (WS) feedstocks

Table 4 Char and volatile matter content of SS, OTP and WS feedstocks

Parameter	SS	OTP	WS
Char content, %	59.2	26.4	24.5
Volatile matter, %	40.8	73.6	75.5

loss observed between 100 and 400 °C, is due to the decomposition of organic compounds. Finally, the weight loss observed above 600 °C is mainly due to the conversion of cellulose and hemi-cellulose into more stable carbon forms and the partial decomposition of inorganic compounds. SS, due to its mineralogical composition, exhibits a significantly lower weight loss (40%), compared to OTP (70%) and WS (80%), as also shown in other studies [71, 72].

The char and the volatile matter (VM) content of the feedstocks after heating to 850 °C, as determined from TG analysis, is shown in Table 4.

Figures 8, 9 and 10 present the SEM backscattered electron images (BSI) of SS, OTP and WS biochars respectively, produced after pyrolysis at 350 °C.

The decomposition of SS biomass pyrolyzed at 350 °C results in a biochar with an undeveloped and heterogeneous structure (Fig. 8a, b) exhibiting several cracks and agglomerates. EDS analysis results on several particles of the SS biochar reveals the presence of elements such as calcium, sodium, iron, potassium, phosphorus, silicon and magnesium, which can directly contribute to soil fertility and thus can be significantly beneficial to plant health [60, 73]. The chemical roughness and surface heterogeneity is probably due to the presence of several mineral phases present in the feedstock and the production of new mineral phases on biochars during pyrolysis. In this context, SEM-EDS analyses revealed the formation of aggregated prismatic crystals of calcium carbonate and fibrous crystals of manganese phosphate on the structure of the produced biochar as shown in Fig. 8c and Fig. 8d, respectively.

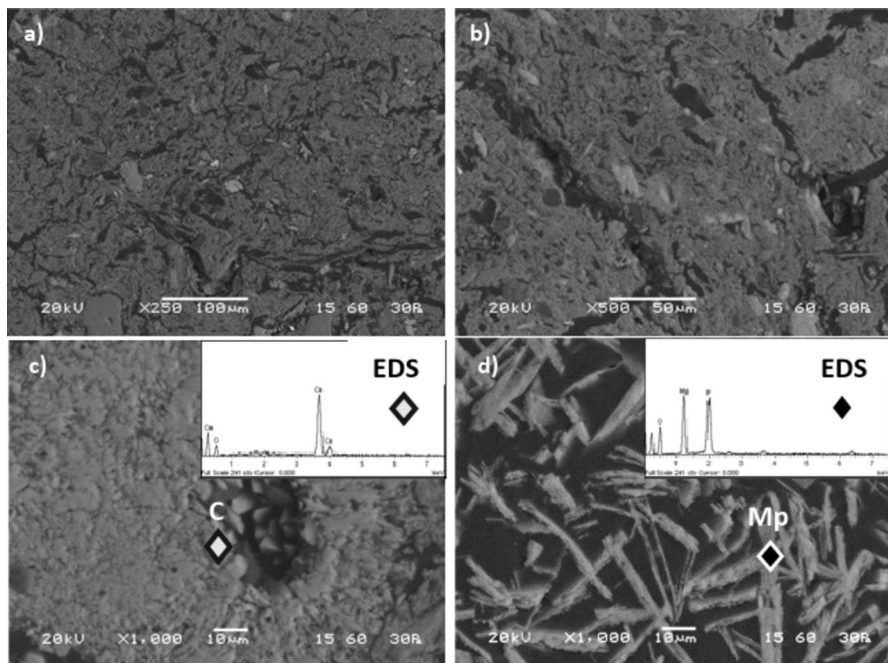


Fig. 8 SEM-BSI images of the SS biochar structures at (a) $\times 250$ and (b) $\times 500$ magnification. Energy dispersive X-ray spectroscopy (EDS) spectra at (c and d) $\times 1000$ magnification show in several spot locations the presence of crystalline phases and newly formed products (C: Calcite, Mp: Magnesium Phosphate)

The OTP biochar obtained after pyrolysis at 350 °C presents a highly porous network comprising numerous cellular microstructures of interconnecting pores along with several notable fibrous microchannels (Fig. 9a, b). The biochar pore size ranges from 1.2 to 17.6 μm , while the average size is 4.5 μm (Fig. 9c); such pore size promotes its capillary water-holding capacity and allows the diffusion of dissolved ions and nutrients through the water-filled pores [74, 75].

In the case of the WS biochar that is produced after pyrolysis at 350 °C, a more continuous structure morphology, compared to OTP and SS biochars, is observed along with a surface area that contains mesopores unevenly spread on the surface (Fig. 10a, c). These mesopores are spherical, ovoid in shape while their size varies from about 18 to 36 μm . Previous studies have shown that biochars with spherical pores exhibit higher adsorption capacity as a result of their capability to easily enlarge their internal porous network after pyrolysis at higher temperature [76–78].

It is evident from these figures that all biochars present a well-defined network of distinct pores and channels suitable for their use as soil amendments and effective adsorbents of contaminants in water and wastewater treatment [79, 80].

Finally, it is underlined that the structure of the different mineral phases present in the initial feedstocks and biochars affect the properties of the substrates, mainly the release of toxic compounds and the availability of nutrients for plants. Biochars may adsorb nutrients and act as slow release fertilizers during irrigation (controlled application of water) of

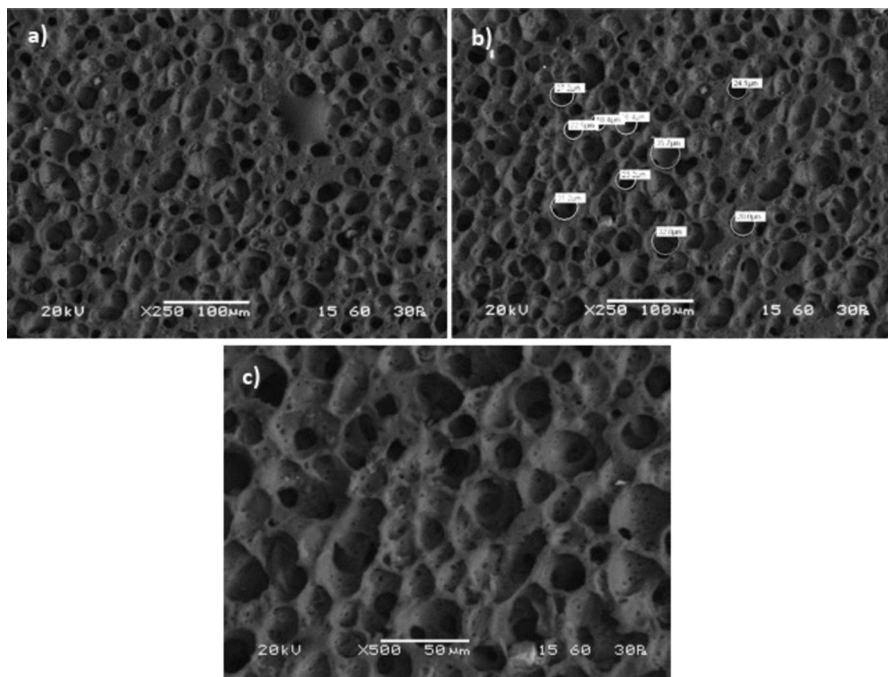


Fig. 10 SEM-BSI images of the WS biochar structures at (a) $\times 250$ magnification, (b) $\times 250$ for measurement of mesopores as well as at (c) $\times 500$ magnification

Table 5 Toxicity of SS, OTP and WS biochars produced at 350 °C—Thresholds (mg/kg) provided by EN 12457–2 test [41], IBI [1], EBC Agro and EBC AgroBio [82]

Element	Biochar type			Thresholds (mg/kg)				
	SS	OTP	WS	EN 12457–2 Inert wastes	EN 12457–2 Non-hazardous wastes	IBI	EBC-Agro	EBC-AgroBio
Cr	4.2	0.2	0.1	0.5	10	93–1200	90	70
Mn	22.6	4.1	1.2	-	-	-	-	-
Ni	2.2	0.2	<DL	0.4	10	47–420	50	25
Cu	8.9	0.9	<DL	2	50	143–600	100	70
Zn	8.6	0.03	<DL	4	50	416–7400	400	200
As	<DL	<DL	<DL	0.5	2	13–100	13	13
Mo	0.1	<DL	<DL	0.5	10	5–100	-	-
Cd	<DL	<DL	<DL	0.04	1	1.4–39	1.5	0.7

IBI International Biochar Initiative, EBC European Biochar Certificate

in nature, comprises $\sim 0.1\%$ of the Earth's crust, has seven oxidation states ranging from -1 to $+7$, and therefore can be easily transferred in biomass and the produced biochars. This is why no thresholds are proposed for Mn by EN 12457 -2 test or IBI and EBC.

The phytotoxicity of biochars as indicated by the values of the germination index (GI) determined for three different seeds (LS, SS, and SC) are presented in Fig. 11. It is known that GI values indicate negative, neutral or positive effect on seed germination in various treatments (i.e., involving different substrates, addition of amendments and presence of

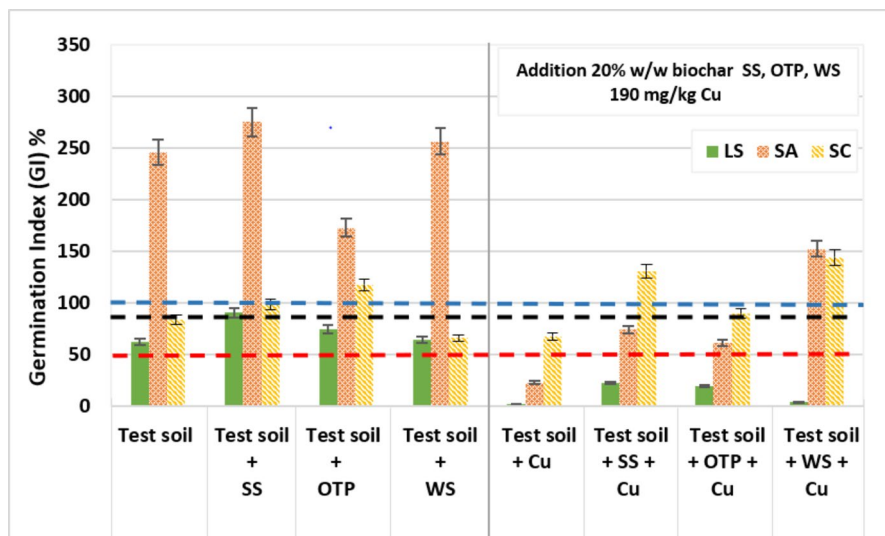


Fig. 11 Germination index for LS, SA and SC seeds in all treatments

chemical substances). Thus, values of the GI higher than 100% indicate that the treatment under study has a clear phytostimulant effect. On the other hand, values between 80% and 100% indicate no phytotoxicity (neutral effect), whereas values between 50 and 80% suggest moderate phytotoxicity and values less than 50% high phytotoxicity [83, 84].

The main conclusions deriving from the data shown in Fig. 11 are:

- the phytotoxicity noticed differs for each seed when biochar or Cu are added in the substrates.
- for *Lepidium sativum* (LS) seeds: a phytotoxic effect is noticed in all treatments, involving addition of biochar and/or contamination of the substrate with 190 mg/kg Cu; in the latter case the GI values are less than 25%.
- for *Sinapis alba* (SA) seeds: the addition of biochar exhibits a clear phytostimulant effect (GI values vary between 170 and 270%); this effect is the most positive among all seeds tested. However, contamination of the substrates with Cu, results in significant inhibition of seed germination, especially when SS and OTP biochars are added in soil. On the other hand, the addition of WS biochar has a clear phytostimulant effect.
- for *Sorghum saccharatum* (SC) seeds: the addition of SS and OTP biochar seems to have a phytostimulant effect. Furthermore, the contamination of the substrate with 190 mg/kg Cu does not seem to affect the germination of the seeds and induces a rather phytostimulant effect.

Overall, the effect of the use of biochar as soil amendment in order to improve plant growth may depend on various factors, as for example, the specific conditions used for the production of biochar, the soil type and quality as well as the type and nutrient needs of the cultivated species. Several studies indicate that biochar improves soil structural and physical characteristics, i.e. pH, EC, specific surface area, water and nutrient retention [85–87].

Conclusions

The present study critically discusses the physico-chemical properties and the morphology of biochars produced from sewage sludge, olive tree pruning and walnut shells, after slow pyrolysis at relatively low temperature, 300–400 °C.

All biochars exhibit alkaline pH, higher than 8.5, and may be used for the buffering of acidity in acidic soils. The specific surface area of the biochars produced at 400 °C ranges between 25 and 45 m² g⁻¹ and indicates that they can be used as adsorbents, slow release fertilisers or soil conditioners. The pyrolysis yield decreases with the increase of pyrolysis temperature and can be as low as 10%; however, the correct pyrolysis temperature is an issue that needs to be determined through a cost – benefit analysis, by taking into account the production cost of the biochar, its yield and its desired properties. SS biochar, with C_{org} content close to 20% is classified as Class III, while OTP and WS biochars with C_{org} content higher than 70 and 80% respectively, are classified as Class I.

SEM analysis indicates that the OTP and WS biochars have a porous network comprising interconnecting pores and fibrous microchannels with mesopores unevenly spread on the surface. On the other hand, the SS biochar has a heterogenous structure with several cracks and agglomerates.

The produced biochars exhibit no toxicity. The leached concentrations of Cr, Ni, Cu and Zn, only from the SS biochar, exceed the thresholds proposed by EN 12457 -2 test for inert wastes but are much lower than the respective thresholds for non-hazardous wastes. On the other hand, the leached concentrations of all elements from all biochars are well below the ranges/thresholds proposed by IBI and EBC.

The phytotoxicity of substrates amended with 20 wt% biochar and/or contaminated with 190 mg/kg Cu, as indicated by the values of the germination index (GI), varies for the three different seeds (LS, SS, and SC) tested. Finally, it is mentioned that the results obtained from the present study are indicative and therefore pilot tests with sufficient duration, i.e. 1–2 cultivation periods, are needed to reliably assess the phytotoxicity of substrates amended with biochar and/or contaminated with heavy metals.

Acknowledgements This work was carried out in the frame of BIOCOM project entitled “Improving soil fertility by combining earthworms and biochars to produce high nutritional and agronomic value products. Implementation of the technology at pilot stage”, <http://biocom.eap.gr>, part of the Agricultural Development Program (RAP) 2014–2022, managed by the General Secretariat of Union Resources and Infrastructure, Special RDP Management Service.

Author contributions Data Curation: VK, DV, AK, GB, Formal Analysis: AK, VK, DV, GB; Methodology: AK, KK, Supervision: AK, KK, Validation: KK, Writing – original draft: AK, VK, DV, Writing, review & editing: GB, KK.

Funding Open access funding provided by HEAL-Link Greece.

Funding was provided by the Special Account of Research (ELKE) of Technical University of Crete (TUC), project No 19201.

Data availability All data is available upon request; please contact the corresponding author.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests On behalf of all authors, the corresponding author states that there is no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. IBI - International Biochar Initiative (2015) Standardized product definition and product testing guidelines for biochar that is used in soil. Canandaigua, NY, USA. https://biochar-international.org/wp-content/uploads/2020/06/IBI_Biochar_Standards_V2.1_Final2.pdf. Accessed 26 October 2024
2. Komnitsas K, Zaharaki D, Pyliotis I, Vamvuka D, Bartzas G (2015) Assessment of pistachio shell Biochar quality and its potential for adsorption of heavy metals. Waste Biomass Valori 6:805–816. <https://doi.org/10.1007/s12649-015-9364-5>
3. Wang B, Gao B, Fang J (2017) Recent advances in engineered Biochar productions and applications. Crit Rev Environ Sci Technol 47:2158–2207. <https://doi.org/10.1080/10643389.2017.1418580>
4. Li M, Tang Y, Ren N, Zhang Z, Cao Y (2018) Effect of mineral constituents on temperature-dependent structural characterization of carbon fractions in sewage sludge-derived Biochar. J Clean Prod 172:3342–3350. <https://doi.org/10.1016/j.jclepro.2017.11.090>
5. Yu D, Niu J, Zhong L, Chen K, Wang G, Yan M, Li D, Yao Z (2022) Biochar Raw material selection and application in the food chain: A review. Sci Total Environ 836:155571. <https://doi.org/10.1016/j.scitotenv.2022.155571>
6. Komnitsas K, Zaharaki D, Bartzas G, Kaliakatsou G, Kritikaki A (2016) Efficiency of Pecan shells and sawdust Biochar on Pb and Cu adsorption. Desalin Water Treat 57:3237–3246. <https://doi.org/10.1080/19443994.2014.981227>
7. Zhang W, Chen R, Li J, Huang T, Wu B, Ma J, Wen Q, Tan J, Huang W (2023) Synthesis optimization and adsorption modeling of Biochar for pollutant removal via machine learning. Biochar 5:25. <https://doi.org/10.1007/s42773-023-00225-x>
8. Spokas KA (2010) Review of the stability of Biochar in soils: predictability of O:C molar ratios. Carbon Manag 1:289–303. <https://doi.org/10.4155/cmt.10.32>
9. Olsson A, Fridahl M, Grönkvist S (2024) Expectations on Biochar as a climate solution in Sweden: carbon dioxide removal with environmental co-benefits. Renew Sustain Energy Transit 5:100087. <https://doi.org/10.1016/j.rset.2024.100087>
10. Hagenbo A, Antón-Fernández C, Bright RM, Rasse D, Astrup R (2022) Climate change mitigation potential of Biochar from forestry residues under boreal condition. Sci Total Environ 807:151044. <https://doi.org/10.1016/j.scitotenv.2021.151044>
11. Li B, Fan CH, Zhang H, Chen ZZ, Sun LY, Xiong ZQ (2015) Combined effects of nitrogen fertilization and Biochar on the net global warming potential, greenhouse gas intensity and net ecosystem economic budget in intensive vegetable agriculture in southeastern China. Atmos Environ 100:10–19. <https://doi.org/10.1016/j.atmosenv.2014.10.034>
12. Cheng N, Peng Y, Kong Y, Li J, Sun C (2018) Combined effects of Biochar addition and nitrogen fertilizer reduction on the rhizosphere metabolomics of maize (*Zea mays* L.) seedlings. Plant Soil 433:19–35. <https://doi.org/10.1007/s11104-018-3811-6>
13. Windeatt JH, Ross AB, Williams PT, Forster PM, Nahil MA, Singh S (2014) Characteristics of biochars from crop residues: potential for carbon sequestration and soil amendment. J Environ Manag 146:189–197. <https://doi.org/10.1016/j.jenvman.2014.08.003>
14. Rafsan N-A-S, Haque SF, Bin, Shah S, Sagues J, Ding R, Ferraris J, Kolar P (2024) Poultry litter-derived Biochar for supercapacitor applications. Next Energy 5:100171. <https://doi.org/10.1016/j.nxen.2024.100171>

15. Mierzwa-Hersztek M, Gondek K, Klimkowicz-Pawlas A, Baran A, Bajda T (2018) Sewage sludge biochars management—Ecotoxicity, mobility of heavy metals, and soil microbial biomass. *Environ Toxicol Chem* 37:1197–1207. <https://doi.org/10.1002/etc.4045>
16. Agraftioti E, Bouras G, Kalderis D, Diamadopoulos E (2013) Biochar production by sewage sludge pyrolysis. *J Anal Appl Pyrol* 101:72–78. <https://doi.org/10.1016/j.jaap.2013.02.010>
17. Zong Y, Wang Y, Sheng Y, Wu C, Lu S (2018) Ameliorating soil acidity and physical properties of two contrasting texture ultisols with wastewater sludge Biochar. *Environ Sci Pollut Res* 25:25726–25733. <https://doi.org/10.1007/s11356-017-9509-0>
18. Gopinath A, Divyapriya G, Srivastava V, Laiju AR, Nidheesh PV, Kumar MS (2021) Conversion of sewage sludge into Biochar: A potential resource in water and wastewater treatment. *Environ Res* 194:110656. <https://doi.org/10.1016/j.envres.2020.110656>
19. Racek J, Sevcik J, Chorazy T, Kucerik J, Hlavinec P (2020) Biochar – Recovery material from pyrolysis of sewage sludge: A review. *Waste Biomass Valori* 11:3677–3709. <https://doi.org/10.1007/s12649-019-00679-w>
20. Zhao L, Sun Z-F, Pan X-W, Tan J-Y, Yang S-S, Wu J-T, Chen C, Yuan Y, Ren N-Q (2023) Sewage sludge derived Biochar for environmental improvement: advances, challenges, and solutions. *Water Res X* 18:100167. <https://doi.org/10.1016/j.wroa.2023.100167>
21. He L, Zhong H, Liu G, Dai Z, Brookes PC, Xu J (2019) Remediation of heavy metal contaminated soils by Biochar: mechanisms, potential risks and applications in China. *Environ Pollut* 252:846–855. <https://doi.org/10.1016/j.envpol.2019.05.151>
22. Junior A, Guo M (2023) Efficacy of sewage sludge derived Biochar on enhancing soil health and crop productivity in strongly acidic soil. *Front Soil Sci* 3. <https://doi.org/10.3389/fsoil.2023.1066547>
23. Lilli MA, Paranychanakis NV, Lionoudakis K, Kritikaki A, Voutsadaki S, Saru ML, Komnitsas K, Nikolaidis NP (2023) The impact of sewage-sludge- and olive-mill-waste-derived Biochar amendments to tomato cultivation. *Sustainability* 15:3879. <https://doi.org/10.3390/su15053879>
24. Berbel J, Posadillo A (2018) Review and analysis of alternatives for the valorisation of agro-industrial Olive oil by-products. *Sustainability* 10:237. <https://doi.org/10.3390/su10010237>
25. Crespo-Barreiro A, Gómez N, González-Arias J, Ortiz-Liébana N, González-Andrés F, Cara-Jiménez J (2023) Scaling-up of the production of Biochar from Olive tree pruning for agricultural use: Evaluation of Biochar characteristics and phytotoxicity. *Agriculture* 13:1064. <https://doi.org/10.3390/agriculture13051064>
26. Abdelhadi SO, Dosoretz CG, Rytwo G, Gerchman Y, Azaizeh H (2017) Production of Biochar from Olive mill solid waste for heavy metal removal. *Bioresour Technol* 244:759–767. <https://doi.org/10.1016/j.biortech.2017.08.013>
27. Marks EAN, Kinigopoulou V, Akrouit H, Azzaz AA, Doulgeris C, Jellali S, Rad C, Sánchez Zulueta P, Tziritis E, El-Bassi L, Matei Ghimbeu C, Jeguirim M (2020) Potential for production of biochar-based fertilizers from Olive mill waste in mediterranean basin countries: An initial assessment for Spain, Tunisia, and Greece. *Sustainability* 12:6081. <https://doi.org/10.3390/su12156081>
28. Azzaz AA, Matei Ghimbeu C, Jellali S, El-Bassi L, Jeguirim M (2022) Olive mill by-products thermochemical conversion via hydrothermal carbonization and slow pyrolysis: detailed comparison between the generated hydrochars and biochars characteristics. *Processes* 10:231. <https://doi.org/10.3390/pr10020231>
29. Adhikari B, Dhungana SK, Waqas Ali M, Adhikari A, Kim I-D, Shin D-H (2019) Antioxidant activities, polyphenol, flavonoid, and amino acid contents in peanut shell. *J Saudi Soc Agric Sci* 18:437–442. <https://doi.org/10.1016/j.jssas.2018.02.004>
30. Pereira JA, Oliveira I, Sousa A, Valentão P, Andrade PB, Ferreira ICFR, Ferreres F, Bento A, Seabra R, Estevinho L (2007) Walnut (*Juglans regia* L.) leaves: phenolic compounds, antibacterial activity and antioxidant potential of different cultivars. *Food Chem Toxicol* 45:2287–2295. <https://doi.org/10.1016/j.fct.2007.06.004>
31. Zhang Z, Liao L, Moore J, Wu T, Wang Z (2009) Antioxidant phenolic compounds from walnut kernels (*Juglans regia* L.). *Food Chem* 113:160–165. <https://doi.org/10.1016/j.foodchem.2008.07.061>
32. Kuśmierek K, Świątkowski A, Dąbek L (2017) Removal of 2,4,6-trichlorophenol from aqueous solutions using agricultural waste as low-cost adsorbents. *Environ Prot Eng* 43. <https://doi.org/10.37190/epel70412>
33. El Mashad HM, Edalati A, Zhang R, Jenkins BM (2022) Production and characterization of Biochar from almond shells. *Clean Technol* 4:854–864. <https://doi.org/10.3390/cleantechnol4030053>
34. El Hamdouni Y, El Hajjaji S, Szabó T, Trif L, Felhósi I, Abbi K, Labjar N, Harmouche L, Shaban A (2022) Biomass valorization of walnut shell into Biochar as a resource for electrochemical simultaneous detection of heavy metal ions in water and soil samples: preparation, characterization, and applications. *Arab J Chem* 15:104252. <https://doi.org/10.1016/j.arabjc.2022.104252>

35. Uslu OS, Babur E, Alma MH, Solaiman ZM (2020) Walnut shell Biochar increases seed germination and early growth of seedlings of fodder crops. *Agriculture* 10:427. <https://doi.org/10.3390/agriculture10100427>
36. Jeníček L, Tunklová B, Malat'ák J, Velebil J, Malat'áková J, Neškudla M, Hnilička F (2023) The impact of nutshell Biochar on the environment as an alternative fuel or as a soil amendment. *Materials* 16:2074. <https://doi.org/10.3390/ma16052074>
37. Alfattani R, Shah MA, Siddiqui MIH, Ali MA, Alnaser IA (2021) Biochar characterization produced from walnut shell biomass through slow pyrolysis: sustainable for soil amendment and an alternate bio-fuel. *Energies (Basel)* 15:1. <https://doi.org/10.3390/en15010001>
38. Mohamed BA, Ellis N, Kim CS, Bi X, Chen W-H (2021) Engineered biochars from catalytic microwave pyrolysis for reducing heavy metals phytotoxicity and increasing plant growth. *Chemosphere* 271:129808. <https://doi.org/10.1016/j.chemosphere.2021.129808>
39. Liu J, Wang J, Lee S, Wen R (2018) Copper-caused oxidative stress triggers the activation of antioxidant enzymes via ZmMPK3 in maize leaves. *PLoS ONE* 13:e0203612. <https://doi.org/10.1371/journal.pone.0203612>
40. Mir AR, Pichtel J, Hayat S (2021) Copper: uptake, toxicity and tolerance in plants and management of Cu-contaminated soil. *Biomaterials* 34:737–759. <https://doi.org/10.1007/s10534-021-00306-z>
41. CEN (2003) EN-12457-2. Characterization of Waste – Leaching – Compliance Test of leaching granular waste materials and sludge – Part 2 – One stage batch test at a liquid to solid ratio of 10 l/kg with particle size below 4 mm (without or with size reduction), Published by DIN on May 1, 2017
42. RIVM, Lijzen JPA, Baars AJ, Otte PF, Rikken MGJ, Swartjes FA, Verbruggen EMJ, van Wezel AP (2001) Technical evaluation of the intervention values for soil/sediment and groundwater, RIVM report 711701023. Rijksinstituut voor Volksgezondheid en Milieu (National Institute of Public Health and the Environment), The Netherlands
43. Yang Y, Wang G, Li G, Ma R, Kong Y, Yuan J (2021) Selection of sensitive seeds for evaluation of compost maturity with the seed germination index. *Waste Manag* 136:238–243. <https://doi.org/10.1016/j.wasman.2021.09.037>
44. Luo Y, Liang J, Zeng G, Chen M, Mo D, Li G, Zhang D (2018) Seed germination test for toxicity evaluation of compost: its roles, problems and prospects. *Waste Manag* 71:109–114. <https://doi.org/10.1016/j.wasman.2017.09.023>
45. Agrafioti E, Kalderis D, Diamadopoulos E (2014) Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *J Environ Manage* 133:309–314. <https://doi.org/10.1016/j.jenvman.2013.12.007>
46. Figueiredo C, Lopes H, Coser T, Vale A, Busato J, Aguiar N, Novotny E, Canellas L (2018) Influence of pyrolysis temperature on chemical and physical properties of Biochar from sewage sludge. *Arch Agron Soil Sci* 64:881–889. <https://doi.org/10.1080/03650340.2017.1407870>
47. Queirós CSGP, Cardoso S, Lourenço A, Ferreira J, Miranda I, Lourenço MJV, Pereira H (2020) Characterization of Walnut, almond, and pine nut shells regarding chemical composition and extract composition. *Biomass Convers Biorefin* 10:175–188. <https://doi.org/10.1007/s13399-019-00424-2>
48. Demirbaş A (2002) Fuel characteristics of Olive husk and Walnut, hazelnut, sunflower, and almond shells. *Energy Sources* 24:215–221. <https://doi.org/10.1080/009083102317243601>
49. Vamvuka D, Alloimonos N (2017) Combustion behaviour of Olive pruning/animal manure blends in a fluidized bed combustor. *Heliyon* 3:e00385. <https://doi.org/10.1016/j.heliyon.2017.e00385>
50. Shetty R, Vidya CS-N, Prakash NB, Lux A, Vaculík M (2021) Aluminum toxicity in plants and its possible mitigation in acid soils by Biochar: A review. *Sci Total Environ* 765:142744. <https://doi.org/10.1016/j.scitotenv.2020.142744>
51. Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS (2009) Impact of Biochar amendment on fertility of a southeastern coastal plain soil. *Soil Sci* 174:105–112. <https://doi.org/10.1097/SS.0b013e3181981d9a>
52. Akhil D, Lakshmi D, Kartik A, Vo D-VN, Arun J, Gopinath KP (2021) Production, characterization, activation and environmental applications of engineered Biochar: A review. *Environ Chem Lett* 19:2261–2297. <https://doi.org/10.1007/s10311-020-01167-7>
53. Zhao B, O'Connor D, Zhang J, Peng T, Shen Z, Tsang DCW, Hou D (2018) Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived Biochar. *J Clean Prod* 174:977–987. <https://doi.org/10.1016/j.jclepro.2017.11.013>
54. Sial TA, Shaheen SM, Lan Z, Korai PK, Ghani MI, Khan MN, Syed A-A, Hussain Asghar Ali MN, Rajpar I, Memon M, Bhatti SM, Abdelrahman H, Ali EF, Rinklebe J, Zhang J (2022) Addition of walnut shells Biochar to alkaline arable soil caused contradictory effects on CO₂ and N₂O emissions, nutrients availability, and enzymes activity. *Chemosphere* 293:133476. <https://doi.org/10.1016/j.chemosphere.2021.133476>

55. Komnitsas K, Zaharaki D, Bartzas G, Alevizos G (2017) Adsorption of scandium and neodymium on Biochar derived after low-temperature pyrolysis of sawdust. *Minerals* 7:200. <https://doi.org/10.3390/min7100200>
56. Vamvuka D, Esser K, Komnitsas K (2020) Investigating the suitability of grape husks Biochar, municipal solid wastes compost and mixtures of them for agricultural applications to mediterranean soils. *Resources* 9:33. <https://doi.org/10.3390/resources9030033>
57. Lilli MA, Paranychianakis NV, Lionoudakis K, Saru ML, Voutsadaki S, Kritikaki A, Komnitsas K, Nikolaidis NP (2023) Characterization and risk assessment of different-origin biochars applied in agricultural experiments. *Sustainability* 15:9036. <https://doi.org/10.3390/su15119036>
58. Oliveira FR, Patel AK, Jaisi DP, Adhikari S, Lu H, Khanal SK (2017) Environmental application of Biochar: current status and perspectives. *Bioresour Technol* 246:110–122. <https://doi.org/10.1016/j.biortech.2017.08.122>
59. Lu H, Zhang W, Wang S, Zhuang L, Yang Y, Qiu R (2013) Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. *J Anal Appl Pyrol* 102:137–143. <https://doi.org/10.1016/j.jaap.2013.03.004>
60. Figueiredo C, Moreira Leão, Vale P-F (2019) Carbon mineralization in a soil amended with sewage sludge-derived Biochar. *Appl Sci* 9:4481. <https://doi.org/10.3390/app9214481>
61. Zielinska A, Oleszczuk P (2016) Effect of pyrolysis temperatures on freely dissolved polycyclic aromatic hydrocarbon (PAH) concentrations in sewage sludge-derived biochars. *Chemosphere* 153:68–74. <https://doi.org/10.1016/j.chemosphere.2016.02.118>
62. Adhikari S, Moon E, Paz-Ferreiro J, Timms W (2024) Comparative analysis of Biochar carbon stability methods and implications for carbon credits. *Sci Total Environ* 914:169607. <https://doi.org/10.1016/j.scitotenv.2023.169607>
63. Sun Z, Hu Y, Shi L, Li G, Pang Z, Liu S, Chen Y, Jia B (2022) Effects of Biochar on soil chemical properties: A global meta-analysis of agricultural soil. *Plant Soil Environ* 68:272–289. <https://doi.org/10.17221/522/2021-PSE>
64. Tan Z, Lin CSK, Ji X, Rainey TJ (2017) Returning Biochar to fields: A review. *Appl Soil Ecol* 116:1–11. <https://doi.org/10.1016/j.apsoil.2017.03.017>
65. Sierra I, Iriarte-Velasco U, Ayastuy JL, Aguayo AT (2023) Production of magnetic sewage sludge Biochar: investigation of the activation mechanism and effect of the activating agent and temperature. *Biomass Convers Biorefin* 13:17101–17118. <https://doi.org/10.1007/s13399-022-02372-w>
66. Park S, Baker JO, Himmel ME, Parilla PA, Johnson DK (2010) Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnol Biofuels* 3:10. <https://doi.org/10.1186/1754-6834-3-10>
67. Sava C, Iluțiu-Varvara D-A, Mare R, Roman MD, Rada S, Pică EM, Jäntschi L (2024) Physico-chemical characterization and possible uses of sludge processed from an urban sewage treatment plant. *Helvion* 10:e29576. <https://doi.org/10.1016/j.helivon.2024.e29576>
68. Albatrni H, Qiblawey H, Al-Marri MJ (2022) Walnut shell based adsorbents: A review study on preparation, mechanism, and application. *J Water Process Eng* 45:102527. <https://doi.org/10.1016/j.jwpe.2021.102527>
69. Cole EJ, Zandvakili OR, Xing B, Hashemi M, Herbert S, Mashayekhi HH (2019) Dataset on the effect of hardwood Biochar on soil gravimetric moisture content and nitrate dynamics at different soil depths with FTIR analysis of fresh and aged Biochar. *Data Brief* 25:104073. <https://doi.org/10.1016/j.dib.2019.104073>
70. Nair RR, Schaate A, Klepzig LF, Turcios AE, Lecinski J, Shamsuyeva M, Endres H-J, Papenbrock J, Behrens P, Weichgrebe D (2023) Physico-chemical characterization of walnut shell Biochar from uncontrolled pyrolysis in a garden oven and surface modification by ex-situ chemical magnetization. *Clean Technol Environ Policy* 25:2727–2746. <https://doi.org/10.1007/s10098-023-02525-z>
71. Magdziarz A, Werle S (2014) Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS. *Waste Manag* 34:174–179. <https://doi.org/10.1016/j.wasman.2013.10.033>
72. Gómez-Rico MF, Font R, Fullana A, Martín-Gullón I (2005) Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content. *J Anal Appl Pyrol* 74:421–428. <https://doi.org/10.1016/j.jaap.2004.11.029>
73. Nicholas HL, Mabbett I, Apsey H, Robertson I (2022) Physico-chemical properties of waste derived Biochar from community scale faecal sludge treatment plants. *Gates Open Res* 6:96. <https://doi.org/10.12688/gatesopenres.13727.2>
74. Sun H, Brewer CE, Masiello CA, Zygorakis K (2015) Nutrient transport in soils amended with Biochar: a transient model with two stationary phases and intraparticle diffusion. *Ind Eng Chem Res* 54:4123–4135. <https://doi.org/10.1021/ie503893t>

75. Verheijen FGA, Zhuravel A, Silva FC, Amaro A, Ben-Hur M, Keizer JJ (2019) The influence of Biochar particle size and concentration on bulk density and maximum water holding capacity of sandy vs sandy loam soil in a column experiment. *Geoderma* 347:194–202. <https://doi.org/10.1016/j.geoderma.2019.03.044>
76. Tran HN, Lee C-K, Nguyen TV, Chao H-P (2018) Saccharide-derived microporous spherical Biochar prepared from hydrothermal carbonization and different pyrolysis temperatures: synthesis, characterization, and application in water treatment. *Environ Technol* 39:2747–2760. <https://doi.org/10.1080/09593330.2017.1365941>
77. Tran HN, Tomul F, Thi Hoang Ha N, Nguyen DT, Lima EC, Le GT, Chang C-T, Masindi V, Woo SH (2020) Innovative spherical Biochar for pharmaceutical removal from water: insight into adsorption mechanism. *J Hazard Mater* 394:122255. <https://doi.org/10.1016/j.jhazmat.2020.122255>
78. Luo R, Li X, Xu H, Sun Y, Wu J (2020) Effects of temperature, solution pH, and ball-milling modification on the adsorption of non-steroidal anti-inflammatory drugs onto Biochar. *Bull Environ Contam Toxicol* 105:422–427. <https://doi.org/10.1007/s00128-020-02948-0>
79. Masud MA, Al, Shin WS, Sarker A, Septian A, Das K, Deepo DM, Iqbal MA, Islam ARMT, Malafaia G (2023) A critical review of sustainable application of Biochar for green remediation: research uncertainty and future directions. *Sci Total Environ* 904:166813. <https://doi.org/10.1016/j.scitotenv.2023.166813>
80. Ashebir H, Nure JF, Worku A, Msagati TAM (2024) Prosopis juliflora Biochar for adsorption of sulfamethoxazole and Ciprofloxacin from pharmaceutical wastewater. *Desalin Water Treat* 320:100691. <https://doi.org/10.1016/j.dwt.2024.100691>
81. Cheng Y, Wu M, Lu J, Li Y, Cai Y, Xiang H, Zhuang Z, Qiu Z, Yu B (2024) Optimizing fabrication of coated fertilizers integrated with Biochar for enhanced slow-release properties: mechanisms and cost-effectiveness analysis. *Ind Crops Prod* 222:120077. <https://doi.org/10.1016/j.indcrop.2024.120077>
82. EBC - European Biochar Certificate (2023) Guidelines for a sustainable production of biochar; Standards International (CSI), Frick, Switzerland. https://www.european-biochar.org/media/doc/2/version_en_10_3.pdf. Accessed 14 October 2024
83. Sobarzo-Bernal O, Gómez-Merino FC, Alcántar-González G, Saucedo-Veloz C, Trejo-Téllez LI (2021) Biostimulant effects of cerium on seed germination and initial growth of tomato seedlings. *Agronomy* 11:1525. <https://doi.org/10.3390/agronomy11081525>
84. Jurado MM, Suárez-Estrella F, Toribio AJ, Martínez-Gallardo MR, Estrella-González MJ, López-González JA, López MJ (2023) Biopriming of cucumber seeds using actinobacterial formulas as a novel protection strategy against *Botrytis cinerea*. *Front Sustain Food Syst* 7. <https://doi.org/10.3389/fsufs.2023.1158722>
85. Belyaeva ON, Haynes RJ, Sturm EC (2012) Chemical, physical and microbial properties and microbial diversity in manufactured soils produced from co-composting green waste and biosolids. *Waste Manag* 32:2248–2257. <https://doi.org/10.1016/j.wasman.2012.05.034>
86. Alburquerque JA, Cabello M, Avelino R, Barrón V, del Campillo MC, Torrent J (2015) Plant growth responses to Biochar amendment of mediterranean soils deficient in iron and phosphorus. *J Plant Nutr Soil Sci* 178:567–575. <https://doi.org/10.1002/jpln.201400653>
87. Milla OV, Chien CC, Huang WJ (2020) The effects of silicon content in rice husk Biochar of Southern Taiwan on the germination of corn seeds (*Zea mays* L). *Open Access J Waste Manag Xenobiot* 3:1–8. <https://doi.org/10.23880/oajwx-16000145>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.