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The Influence of Biochar and Solid Digestate on Rose-Scented Geranium (*Pelargonium graveolens* L'Hér.) Productivity and Essential Oil Quality

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Abstract: In recent years, biochar has generated global interest in the areas of sustainable agriculture and climate adaptation. The main positive effects of biochar were observed to be the most remarkable when nutrient-rich feedstock was used as the initial pyrolysis material (i.e., anaerobic digestate). In this study, the influence of solid anaerobic digestate and biochar that was produced by the slow pyrolysis of solid digestate was evaluated by comparing the differences in the crop growth performances of *Pelargonium graveolens*. The experiment was conducted in a greenhouse while using three different growth media (i.e., solid digestate, biochar, and vermiculite). The results indicated that: (i) the pyrolysis of solid digestate caused a reduction in the bulk density (−52%) and an increase in the pH (+16%) and electrical conductivity (+9.5%) in the derived biochar; (ii) the best crop performances (number of leaves, number of total branches, and plant dry weight) were found using biochar, particularly for plant dry weight (+11.4%) and essential oil content (+9.4%); (iii) the essential oil quality was slightly affected by the growth media; however, the main chemical components were found within the acceptable range that was set by international standard trade; and, iv) biochar induced the presence of leaf chlorosis in *Pelargonium graveolens*.

Keywords: biochar; solid digestate; *Pelargonium graveolens*; leaf chlorosis; essential oil quality

1. Introduction

In recent decades, biochar, a carbon-rich product that is generated by pyrolysis of biomass under anaerobic conditions [1], has garnered much interest as a soil amendment. Nevertheless, several studies report contrasting results when biochar is incorporated in the potting substrates [2,3] or in open soil systems [4].

Among the numerous positive effects of biochar, the improvement of the soil water-holding capacity, increased aeration and cation exchange capacity (CEC), liming the potential, and increased nutrient availability are among the most relevant ones [5–8]. Furthermore, biochar contributes to carbon sequestration, thanks to its high stability and resistance to biological degradation, thus contributing to climate change mitigation, i.e., reducing agricultural greenhouse gas emissions [1,9]. Nonetheless, despite the aforementioned positive properties, biochar application in agricultural soils could potentially generate risks of increased concentrations of pollutants and toxic compounds, such as heavy metals, polyhydroxyalkanoates (PHAs), etc., thus promoting their incorporation in the soil [10]. In fact, as biochar is obtained by heating the biomass in the complete absence of oxygen, tars are

generated, and could condense onto the biochar; moreover, if biomass contains heavy metals, these will be retained in the solid matter [11]. The method through which biochar is produced and extracted by the plant, together with the type of feedstock, will determine the different characteristics of the carbonized products.

The chemical and physical biochar characteristics depend on the initial structure of the lignocellulosic biomass (i.e., woods and barks, agricultural wastes, green-waste, and animal manures) and process conditions (i.e., type of pyrolysis, heating rate, maximum temperature and holding time at maximum temperature, biochar extraction, and condensation of volatiles), which thus result in mixed and contrasting outcomes regarding the promotion of soil fertility [12]. Generally, biochar that is produced from nutrient-rich feedstock, such as crop residues, manures, and anaerobic digestion residues (i.e., digestate) possesses higher nutrient contents than biochar that is generated from nutrient-poor feedstock (i.e., wood residues), which, in turn, determines lower soil benefits due to lower mineralization rates [6,13].

The anaerobic fermentation process is considered as being one of the most environmentally friendly methods to convert organic material, such as municipal solid wastes, manures, energy crops, and agricultural residues, into biogas, an energy-rich product. The degradation process takes place in biogas plants under optimal conditions (temperature, mixing, pH, etc.) and it is driven by a microbial consortium [14,15]. Digestate by-product, which is characterized by a nutrient-rich and homogeneous mixture of microbial biomass and undigested material, is usually used as fertilizer for supplying nutrients [15]. Moreover, digestate can be mechanically separated into liquid (80–90%) and solid fractions (10–20%), in order to facilitate the storage, handling, transport, and discharge [14]. As digestate is produced in large quantities throughout the year, it is often stored and distributed on soils only during dry days in order to avoid nutrient leaching [8]. The pyrolysis of digestate can generate biochar with a higher cation exchange capacity and higher phosphorous concentration when compared to the initial material and other feedstock [13–16].

The objectives of this study were: (i) the characterization of biochar as derived from solid digestate and the initial feedstock; (ii) the determination of the physical–chemical characteristics of the growth media after addition of soil amendments; and, (iii) evaluation of the growth-media-induced influence on yield, growth, and oil quality in rose-scented geranium (*Pelargonium graveolens* L'Hér.) cultivation.

The crop, which belongs to the *Geraniaceae* family, is an important aromatic plant that is cultivated in several countries (e.g., Algeria, Egypt, Morocco, Madagascar, France, China, and India) for the extraction of essential oil (EO), widely used in the perfumery, cosmetic, pharmaceutical, and food industries [17–19], and chosen because of its sensitivity to growth when it is cultivated using different substrates [20,21].

2. Materials and Methods

2.1. Description of Substrates and Their Components

The substrates were generated by mixing three different components: solid digestate, biochar, and vermiculite. (i) Solid digestate was obtained from thermophilic anaerobic digestion of corn silage, manure, and vegetable waste, in a biogas plant that is located in Ravenna (Italy). The samples were collected during spring 2016 and air-dried at 25 °C for two weeks before use. (ii) Biochar was obtained by slow pyrolysis in a pilot unit, fed with the digestate. The biomass in the pyrolyser was continuously mixed by rotating paddles. Carbonization was carried out at a temperature of 500 °C for 3 h, under a continuous flow of N_2, continuous extraction of pyrogases, and a heating rate of 25 °C/min. At the end of the set reaction time, the reactor was left to cool down to ambient temperature (continuing the extraction of pyrogases) overnight and then the biochar was extracted. The process yield (33.6%) was calculated from triplicate samples and expressed as weight percentages of dry weight biochar recovered to dry weight initial biomass, according to Vaughn et al. [22]. (iii) The vermiculite, which was used as a neutral filler component, was composed of particle sizes with diameters of 2–5 mm.

The three growth media were prepared by mixing all of the components. The products were differentiated, as follows: control (CS): vermiculite 100%; biochar substrate (BCS): vermiculite and biochar in a ratio 2:1 by volume; solid digestate substrate (SDS): vermiculite and solid digestate in a ratio of 2:1 (*v*:*v*).

In setting up the trial, growth media and primary components were chemically and physically characterized. The samples (three replicates) of each growth media were previously dried at 30–35 °C for six days, ground in a ceramic mortar, and sifted through a 2 mm sieve. The total C, H, N, and S contents were determined using a CHNS analyzer (LECO Corp. St. Joseph, MI, USA) following the American Society for Testing and Materials (ASTM) method D5373, while the elemental composition (As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, and Zn) was detected using an Inductively-Coupled Plasma Optical Emission Spectrometer (ICP, model IRIS Intrepid II XSP Radial, Thermo Fisher Scientific, Waltham, MA, USA), according to the EPA Method SW6020. Electrical conductivity (EC) and pH were measured following Ahmedna et al. [23] in water extracts (sample: deionized water ratio of 1:1, *w*/*w*) by employing a portable EC meter (Hanna Instruments HI 9313-6, Rhode Island, USA) and a pH meter (pHenomenal pH 1100L, VWR International, Leuven, Germany).

The physical properties (i.e., bulk density, total porosity, container capacity, and air space) were determined by using the ring knife method [24]. A ring knife with a volume of 200 cm^3 and weight W_0 was filled with the air-dried sample and weighed (W_1). Afterwards, the sample was saturated with distilled water for 24 h and weighed again (W_2). The ring knife with the saturated sample was opened from one side and then placed upside down on a holder with a leaky screen until the water stopped dripping from the bottom for 3 h before the ring knife and sample were weighed (W_3). Finally, the oven dried sample and the ring knife were kept at 65 °C until a constant weight was reached and weighed (W_4). The physical characteristics were calculated while using the following formulas: bulk density (g cm^{-3}) = $(W_4 - W_0)/200$; total porosity (%) = $(W_2 - W_4)/200 \times 100$; air space (%) = $(W_2 - W_3)/200 \times 100$; and, container capacity (%) = total porosity − air space.

2.2. Experimental Design

The experiment was carried out in a greenhouse that was located at the University of Florence (Italy). Plants of rose-scented geranium (*Pelargonium graveolens*) were cloned by first obtaining tissue culture from the same mother plant native to Madagascar using the methods reported by Grassi et al. [25]. After seven months of in-vitro cultivation, plantlets of about 10 cm in height, with seven leaves, and well-developed rooting systems were transplanted into 2 L plastic pots containing the experimental substrates.

A total of 21 pots for each growth medium were prepared and arranged in a randomized complete block design (RCBD) with three replicates. The pots were placed at 60 cm from each other between rows and at 30 cm from each other within a row, similar to the optimum plantation density in an open field [14]. The trial was conducted during the spring–autumn season (July–September), where the maximum and minimum temperatures were 29.8 °C and 17.0 °C, respectively. Within each treatment, five pots were randomly selected and equipped with a soil moisture sensor. An automated irrigation scheduling program was set up to maintain the soil moisture content at 60%, and thus avoid water stress.

2.3. Sampling and Plant Analysis

The biomass was harvested 70 days after transplanting, during the early flowering stage (i.e., balsamic time) in order to simulate the common cultivation practice. Cutting the flowers' stems and leaving 1–2 growing buds for the subsequent regeneration harvested the plants [18]. All of the vegetative parameters, such as plant height, number of leaves, number of principal branches, number of total branches, plant dry weight, and a soil plant analysis development (SPAD) chlorophyll meter were collected and recorded at the time of harvest. Three fully expanded and healthy leaves (top, middle, and bottom of the plant height) were collected for each plant at harvest time, dried in

oven at 65 °C, ground in a ceramic mortar, and sifted through a 2 mm sieve in order to determine the nutrient concentration in biomass. The concentrations of macro and micro-nutrients were determined according to the CHNS and ICP methods.

2.4. Essential Oil Extraction and GC–MS Analysis

The EO extraction was performed while using the hydro-distillation method using a Clevenger apparatus (Ambala Cantt, Haryana, India) [26]. The distilled EO of each sample was filtered, dehydrated with anhydrous sodium sulfate, and stored at 0 °C until analyzed. The essential oil yield (EO%) of the distilled biomass was obtained as the percentage on a volume basis (ml oil extracted from 100 g dry plant herbage), while the essential oil content for each plant (EOpl) was calculated by multiplying the EO% for the biomass weight and expressed in g oil/plant. GC–MS analysis was performed on a PerkinElmer 8500 gas chromatograph (Perkin–Elmer, Norwalk, CT, USA), which was equipped with a fused silica column BP1 25 m, 0.5 mm, and ID 25 µm. The column was programmed from 60 to 250 °C at a rate of 5 °C min^{-1} and the maximum temperature was maintained for 5 min. The injection and detector temperatures were 250 °C and 300 °C, respectively. Nitrogen (1.1 mL min^{-1}) was used as the carrier gas and the split ratio was 1:50. Compound identification was performed by comparing the retention times of spectral peaks using the NIST08 library database, and then the corresponding Kovats index was calculated.

2.5. Statistical Analysis

Statistical analysis was performed using IBM SPSS Statistics v.21 software (IBM Corp., New-York, NY, USA). Analysis of variance (ANOVA) was used to detect the significance of the effects of the treatments on the vegetative parameters and nutrient content in plants. Data that did not fulfill ANOVA assumptions were the arcsin square root that was transformed before running the model. The most significant parameters that were identified by ANOVA were successively analyzed using a post hoc Tukey's test implemented using the same software.

3. Results

3.1. Characterization of Digestate and Biochar

Table 1 reports the chemical and physical properties of biochar and its initial feedstock (solid digestate). The solid digestate fraction had a pH of 7.1 and EC value of 6.21 mS cm^{-1}. The pyrolysis process resulted in an increase of about one pH unit (8.5) and a slight increase in the EC value, reaching 6.86 mS cm^{-1}. An increase in several of the macro and micro-element contents was observed in the biochar with respect to the solid digestate. The only exception was observed for S content, which was totally absent in biochar. Specifically, biochar showed an increase in N (+11%), P (+41%), and K (+41%) contents when compared to solid digestate, and a large amount of Fe, Mn, and Na (i.e., 1935.00, 454.60, and 1235.00 mg kg^{-1}), with respect to the initial material (i.e., 998.74, 168.80, and 827.00 mg kg^{-1}). The carbon content (C) increased, from 39.8% in the digestate to 55.83% in biochar. The pyrolysis process also affected the bulk density, which shifted from 0.29 kg m^{-3} in solid digestate to 0.14 kg m^{-3} in the pyrolyzed product.

3.2. Characterization of Growth Media

Biochar and solid digestate influenced the main chemical and physical properties of the growth media (Table 1). BCS showed the highest pH value (7.8), followed by SDS (6.7) and CS (5.6). Regarding EC data, the substrate added with biochar (BCS) exhibited a slightly higher value (2.11 mS cm^{-1}) than SDS (1.98 mS cm^{-1}) and CS (1.79 mS cm^{-1}). The bulk density and air space yielded the highest values in SDS (0.16 kg m^{-3} and 29.6%, respectively), followed by BCS (0.11 kg m^{-3} and 27.4%, respectively) and CS (0.09 kg m^{-3} and 23.3%, respectively). By contrast, CS recorded the highest values for the

container capacity (65.5%) and total porosity (88.8%). The macro and microelement contents were highest in BCS, whilst lower values were found in SDS and CS.

Table 1. Physical–chemical properties of organic material and growth media used in *P. graveolens* cultivation. All values are means of three replicates ± standard deviation. Solid digestate; biochar; SDS (Solid Digestate Substrate); BCS (Biochar Substrate); CS (Control Substrate).

Parameters	Primary Components		Growth Media		
	Solid Digestate	Biochar	SDS	BCS	CS
pH	7.1 ± 0.12	8.5 ± 0.07	6.7 ±0.09	7.8 ± 0.08	5.6 ± 0.09
EC (mS cm^{-1})	6.21 ± 0.03	6.86 ± 0.09	1.98 ± 0.02	2.11 ± 0.03	1.79 ± 0.04
Bulk density (kg m^{-3})	0.29 ± 0.04	0.14 ± 0.10	0.16 ± 0.02	0.11 ± 0.06	0.09 ± 0.10
Air space (%)	NA	NA	29.60 ± 1.71	27.40 ± 2.11	23.30 ± 0.89
Container capacity (%)	NA	NA	50.20 ± 0.11	56.80 ± 1.01	65.50 ± 0.65
Total porosity (%)	NA	NA	79.80 ± 0.78	84.20 ± 0.29	88.80 ± 0.57
C (%)	39.80 ± 0.23	55.83 ± 0.64	16.11 ± 0.58	19.01 ± 0.03	13.91 ± 0.09
H (%)	5.68 ± 1.14	2.03 ± 0.99	0.91 ± 0.68	0.94± 0.12	0.83 ± 0.28
N (%)	1.23 ± 1.18	1.46 ± 0.97	0.72 ± 1.89	0.84 ± 0.95	0.05 ± 1.06
S (%)	0.29 ± 0.09	ND	ND	ND	ND
K (%)	1.41 ± 1.03	3.43 ± 0.41	1.15 ± 0.83	2.53 ± 0.67	0.65 ± 0.76
P (%)	0.79 ± 0.51	1.91 ± 0.09	0.47 ± 0.52	0.71 ± 0.29	0.15 ± 0.38
Ca (%)	2.00 ±0.39	3.93 ± 0.87	2.22 ± 0.74	2.91 ± 0.03	1.76 ± 0.26
Mg (%)	0.47 ± 0.21	0.95 ± 0.27	2.61 ± 0.63	2.69 ± 0.11	2.86 ± 0.18
As (mg kg^{-1})	4.56 ± 0.03	8.03 ± 0.29	8.67 ± 0.07	8.78 ± 0.37	8.99 ± 0.09
Ba (mg kg^{-1})	15.54 ± 0.19	35.53 ± 0.12	256.15 ± 0.16	262.90 ± 0.23	319.61 ± 0.31
Cd (mg kg^{-1})	0.05 ± 0.22	0.28 ± 0.7	0.43 ± 0.81	0.50 ± 0.29	0.43 ± 0.41
Cr (mg kg^{-1})	7.53 ± 1.14	14.15 ± 1.28	59.47 ± 0.03	83.66 ± 0.07	79.04 ± 0.56
Cu (mg kg^{-1})	30.37 ± 2.12	61.52 ± 3.47	69.13 ± 2.93	72.41 ± 4.29	89.12 ± 3.49
Fe (mg kg^{-1})	998.74 ± 0.04	1935.00 ± 0.02	680.21 ± 0.14	880.36 ± 0.75	553.02 ± 0.39
Mn (mg kg^{-1})	168.60 ± 0.17	454.60 ± 0.64	356.50 ± 0.21	429.60 ± 0.22	431.80 ± 0.28
Na (mg kg^{-1})	827.00 ± 0.56	1235.00 ± 0.49	1675.00 ± 0.79	1848.00 ± 0.11	1704.00 ± 0.23
Ni (mg kg^{-1})	3.94 ± 0.03	10.58 ± 0.49	40.35 ± 0.87	42.45 ± 0.76	58.35 ± 0.24
Pb (mg kg^{-1})	1.92 ± 0.98	6.07 ± 1.68	50.43 ± 3.21	56.86 ± 3.23	43.01 ± 2.47
Zn (mg kg^{-1})	170.70 ± 0.86	380.70 ± 0.91	166.80 ± 0.49	228.40 ± 0.73	85.40 ± 0.55

Note: NA, not available; ND, not detectable.

3.3. Effect on Vegetative Parameters and Foliar Nutrient Content

Table 2 displays the growth media effects on vegetative parameters. Overall, the number of total branches, plant dry weight, and SPAD showed high statistical significance ($p < 0.01$), whilst the number of leaves and number of principal branches were less influenced by the substrates ($p < 0.05$). No statistical significance ($p > 0.05$) was found for plant height.

Using BCS, all of the parameters were significantly higher than those that were found in SDS and CS, with the exception of the SPAD parameters. On average, plants that were cultivated under BCS had about 146 leaves, 2.5 principal branches, 16 total branches, a dry weight of 122.7 g, and a SPAD value of 17.89. Using SDS, the most important decrease was found in the plant dry weight (−11.4%), thus reflecting the lower total number of branches (−41.6%) and leaves (−13.3%) when compared to BCS. By contrast, an increase was observed in SPAD (+42.7%). The lowest performances were observed under CS. Considerable reductions as compared to BCS were found in the number of leaves (−28%) and plant dry weight (−67.5%). SPAD showed an increase of about 40%.

Leaf decoloration was also observed when BCS was used. This condition was indicated by SPAD (17.9), which was much lower when compared to SDS (31.2) and CS (29.8).

Differences in growth media also significantly affected the accumulation of leaf nutrients (Table 3). In particular, plants that were cultivated in BCS showed the highest content in C (41.9%), N (2.2%), P (0.4%), K (3%), Fe (184.7 mg kg^{-1}), and Mn (79.4 mg kg^{-1}). Conversely, considerable decreases in

nutrient contents were observed both using SDS and CS, particularly for Fe (−49% using SDS) and Mn (−70% using CS).

Table 2. Effects of growth media on vegetative parameters and essential oil response in *P. graveolens* cultivation. All the values are means of three replicates ± standard deviation. SDS, solid digestate growth media; BCS, biochar growth media; CS, control growth media; SPAD, soil plant analysis development; EO, essential oil.

Vegetative Parameters	Growth Media		
	SDS	BCS	CS
Plant height (cm)	33.90 ± 2.91 a	34.91 ± 3.09 a	35.10 ± 3.20 a
Number of leaves	126.81 ± 9.31 ab	146.23 ± 14.32 a	105.62 ± 7.59 b
Number of principal branches	2.33 ± 1.02 a	2.55 ± 0.89 a	1.71 ± 0.64 b
Number of total branches	9.38 ± 3.76 b	16.05 ± 5.06 a	8.24 ± 2.96 b
Plant dry weight (g)	108.67 ± 5.74 ab	122.70 ± 6.31 a	82.81 ± 4.49 b
SPAD	31.22 ± 4.37 a	17.89 ± 2.68 b	29.80 ± 5.19 a
EO Parameters	**Growth Media**		
	SDS	**BCS**	**CS**
Oil yield (%)	0.126 ± 1.15 a	0.122 ± 0.40 a	0.133 ± 0.63 a
Oil content (g)	0.136 ± 0.98 ab	0.150 ± 0.56 a	0.110 ± 1.02 b

Note: means followed by common letters within the same row are not significantly different ($p > 0.05$).

Table 3. Foliar nutrient content in a *P. graveolens* plant grown in different growth media. All values are means of three replicates ± standard deviation. SDS, solid digestate growth media; BCS, biochar growth media; CS, control growth media.

Elements	Units	Growth Media		
		SDS	BCS	CS
C	(%)	40.83 ± 1.51 a	41.94 ± 1.16 a	36.46 ± 0.88 b
H	(%)	7.36 ± 1.71 a	7.74 ± 2.01 a	7.05 ± 1.46 a
N	(%)	1.75 ± 0.63 ab	2.16 ± 0.88 a	1.23 ± 1.37 b
S	(%)	0.07 ± 0.33 a	0.08 ± 0.10 a	0.05 ± 0.54 a
K	(%)	1.57 ± 2.11 b	3.01 ± 0.49 a	1.33 ± 0.69 b
P	(%)	0.21 ± 1.36 ab	0.38 ± 1.76 a	0.10 ± 0.86 b
Ca	(%)	2.97 ± 0.10 a	3.73 ± 0.44 a	2.41 ± 0.46 a
Mg	(%)	0.41 ± 0.17 a	0.54 ± 0.27 a	0.35 ± 0.19 a
As	(mg kg^{-1})	2.13 ± 0.92 a	1.52 ± 0.41 a	0.89 ± 0.25 a
Ba	(mg kg^{-1})	24.06 ± 2.09 a	23.05 ± 1.87 a	26.50 ± 1.21 a
Cd	(mg kg^{-1})	ND	ND	ND
Cr	(mg kg^{-1})	0.47 ± 0.32 a	0.94 ± 0.13 a	0.88 ± 0.22 a
Cu	(mg kg^{-1})	3.30 ± 0.74 a	4.19 ± 0.93 a	3.78 ± 0.59 a
Fe	(mg kg^{-1})	90.32 ± 1.06 b	184.74 ± 1.50 a	90.93 ± 0.98 b
Mn	(mg kg^{-1})	43.39 ± 1.49 b	79.35 ± 1.32 a	23.32 ± 1.39 b
Na	(mg kg^{-1})	238.78 ± 0.13 a	235.26 ± 0.37 a	190.36 ± 0.28 b
Ni	(mg kg^{-1})	1.08 ± 0.06 a	1.41± 0.08 a	2.40 ± 0.04 a
Pb	(mg kg^{-1})	0.11 ± 0.35 a	0.14 ± 0.16 a	0.35 ± 0.98 a
Zn	(mg kg^{-1})	42.70 ± 0.75 a	38.88 ± 0.51 a	29.17 ± 0.43 b

Note: ND, not detectable. Means followed by common letters within the same row are not significantly different ($p > 0.05$).

3.4. Effect on Essential Oil Yield and Quality

Essential oil yield (EO%) was similar in plants that were cultivated in CS (0.13%), SDS (0.13%), and BCS (0.12%) (Table 2), while the essential oil content (EOPl) was higher in BCS (0.15 g/plant) as compared to that found in SDS (0.14 g/plant) and in CS (0.11 g/plant).

The GC–MS analysis (Table 4) of essential oil showed that the five most represented chemical oil components were: citronellol (27.9–33.2%), citronellyl formate (15–17%), geraniol (13.8–15.6%), isomenthone (4.4–5.4%), and linalool (2.4–3.1%). Among these, only citronellol and geraniol appear to be influenced by the growth media, with CS possessing the highest content of geraniol (33.2%) and the lowest content of citronellol (13.8%). Finally, the values of the citronellol/geraniol ratio were 1.8, 2.1, and 2.4 using BCS, SDS, and CS, respectively.

Table 4. The effects of growth media on the main chemical components of essential oil in *P. graveolens* cultivation. All values are means of three replicates ± standard deviation. SDS, solid digestate growth media; BCS, biochar growth media; CS, control growth media.

Parameters	Units	Growth Media		
		SDS	BCS	CS
Linalool	(%)	3.04 ± 0.16 a	2.39 ± 0.09 a	3.07 ± 0.10 a
Isomenthone	(%)	4.38 ± 0.06 a	5.41 ± 0.02 a	5.36± 0.01 a
Citronellol	(%)	30.2 ± 0.56 ab	27.86 ± 0.19 b	33.18 ± 0.29 a
Geraniol	(%)	14.28 ± 0.88 ab	15.62 ± 0.37 a	13.76 ± 0.48 b
Citronellyl formate	(%)	15.87 ± 0.03 a	16.95 ± 0.34 a	14.99 ± 0.09 a
C/G ratio		2.11	1. 78	2.41

Note: means followed by common letters within the same column are not significantly different ($p > 0.05$).

4. Discussion

4.1. Characterization of Digestate and Biochar

The pH increases that were observed during the pyrolysis process are coherent with the findings of Enders et al. [27], who observed that biochar deriving from animal manures (e.g., dairy manure, poultry manure, digested dairy manure, composted dairy manure), annual crop residues (corn, grass clippings, leaves), and waste leads to pH values that are generally above 7.5. These increases were likely due to the rapid rate of carbonization and the concentration of basic inorganic compounds [28–30]. Stefaniuk and Oleszczuk [30] reported higher pH values (i.e., >10) in the solid digestate fraction that was processed at 500 °C with respect to what is reported in this study. This was likely due to a longer pyrolysis time (5 h) when compared to that adopted in this study (3 h). This finding proposes the application of biochar that is produced by prolonged pyrolysis processes as a smart solution for soil pH re-equilibration and for alleviating nutrient stress on plant growth in areas that are characterized by acidic soils [31,32].

The increases of EC occurred during the thermal conversion process, a phase where chemical compounds responsible for salinity (i.e., production of K, Na, Mg, and Ca) are accumulated [33]. The EC values that were found in the three growth media were within the range of 0.007 and 8.3 mS cm^{-1} [16,28], thus they were below the threshold that was considered to be limiting for plant growth [34]. By contrast, when the pyrolysis of unseparated digestate produces biochar with higher EC values (>19.00 mS cm^{-1}), the addition of biochar to the soil should be carefully done in order to reduce the risks of salinity stress, which may negatively impact plant growth, root development, and soil macro and microorganisms [30,35,36].

As observed using other nutrient-rich feedstocks (i.e., sewage sludge, raw food waste, and food waste), the bulk density of solid digestate decreases upon pyrolysis [37,38]. In this study, the observed biochar bulk density was in the range that was reported by literature (0.08 to 0.8 kg m^{-3}) [22,38,39]. The pyrolysis process decreases the bulk density of the feedstock and increases biochar porosity at high process temperatures [40]. Biochar can be used for increasing soil aeration, facilitating root growth, promoting microbial respiration activity, and enhancing soil aggregate formation [5], thereby improving crop performances.

The contents of chemical elements found in biochar were mainly related to the process temperature [16]. Pyrolysis reduces mass, which thus enriches the concentration of chemical elements [41]. In our study, where pyrolysis occurred at a temperature of 500 °C for 3 h (slow pyrolysis), the considerable C increase (+71%) was associated with the loss of the hydroxyl group by dehydration [13,16]. A similar C increase was also observed in biochar that was obtained from digested sugarcane bagasse, agricultural residues, and anaerobic digestate [8,13]. By contrast, Garlapalli et al. [29], while using digestate in a pyrolysis process characterized by a short reaction time and higher temperatures, reported higher elemental carbon content (89%). This different process, despite producing a lower biochar yield, allows for higher fixed carbon and lower ash contents to be obtained, thus improving its mitigative potential due to a higher resistance to biotic degradation [28,29,42].

The results also indicated an N-content increase from solid digestate to biochar. This pattern had already been observed by Pituello et al. [16]; they reported that using silage digestate and pruning residues at temperatures below 550 °C caused an increase in the N content due to the formation of aromatic and heterocyclic structures. However, the different feedstocks also determine the N content in biochar. For instance, Tian et al. [43] observed a decrease in the N content (NO_x and NH_3) using sewage sludge coupled with cracking reactions of nitriles, N-heterocyclic compounds, and polymerization of amine-N when the pyrolysis temperature was between 300 to 700 °C.

The concentration of other inorganics in biochar (P, K, Ca, Mg, Fe, Zn) was probably due to the low volatility of their oxides, leading to gradual volatilization of oxygen and hydrogen [44]. This phenomenon was also observed in other studies during the pyrolysis of feedstocks as wastewater sludge, manure, and algae [33,45,46]. Stefaniuk and Oleszczuk previously highlighted the absence of S in biochar [30], who observed a decomposition of the sulfur-containing compounds into volatile SO_2 during the thermal process [44]. The highest presence of individual chemical elements in biochar was likely due to the more nutrient-rich feedstock as compared with the raw material (i.e., wood residues) used for the common biochar production [6]. The range of these elements was within the range that was suggested by the European Biochar Certificate (EBC) [47].

4.2. Characterization of Growth Media

Changes in the growth media properties after the addition of biochar and solid digestate were in the range that was suggested for the amendment to soil use [48]. However, the main changes were observed in soil pH. In SDS and CS, the pH fell within the optimum range indicated for the *Geraniaceae* family (5.7–6.6) [49]. By contrast, in BCS, the pH exceeded the optimal range, which was likely due to the presence of alkaline inorganic components [8].

However, the analysis of plant performances did not show any reduction on the vegetative parameters (i.e., plant height, plant dry weight, etc.). Ram et al. [50], who reported a similar herbage yield in *P. graveolens* cultivation, even when the pH was outside the optimal range (i.e., 4.9 and 8.4), also noted this. In a more recent study, Ram et al. [18] highlighted the lack of symptoms of nutrient deficiency or toxicity in growth media at a pH of 8.1. Other biochar properties that were not considered in this study (i.e., CEC, surface area, porosity) may have a hidden possible negative effect on the crop growth parameters.

4.3. Effect on Vegetative Parameters

The influence of growth media on vegetative parameters of *P. graveolens* showed that the highest performances were found using BCS. This result was partly expected, since BCS showed the highest nutrient availability, which favored biomass growth, herb yield, plant height, and leaf area in *P. graveolens* [5,18,20,21,51].

Under BCS, the high amount of different heavy metals, which are widely acknowledged as promoters of oxidative stress that is highly detrimental to cellular function and metabolism [52], did not negatively influence biomass or organ size. These results are in contrast with the findings of Patel and Patra [53], who, in *P. graveolens*, observed decreases in plant height and leaf area with concurrent

increases in the content of heavy metals. Regarding the production of essential oil, the use of BCS increased the total biomass, particularly the size of the leaves and branches, which increases the yield of essential oil due to a higher presence of glandular trichomes [54].

4.4. Foliar Nutrient Composition

The foliar nutritional content was significantly influenced by the different growth media (Table 3). The high nutrients content (P, K, Ca, Mg, Na, Fe, Cu, Zn) that was found using biochar has also been reported by Awad et al. [51] for vegetables that were cultivated under a hydroponic system, and by Lehmann et al. [55] in cowpea and rice in Brazilian soils. However, when biochar exceeds the optimal rate, a reduction in the uptake of nutrients with a consequent decrease in biomass production can be observed. For instance, Conversa et al. [56] suggested that, in *P. zonale*, the application of biochar should not exceed 70:30 (v/v) in the peat/biochar substrate mixture. This is highly important, especially when considering the essential oil production, where a decrease in biomass may have negative economic consequences. Nevertheless, the processes governing biomass reduction are still unclear. Some studies [5,35] have suggested that this may be due to several interactions between biochar, plant roots, and microorganisms in the rhizosphere or complex reactions, depending on the properties of the soils and biochar involved. Despite awareness of these relationships, these mechanisms are still far from being completely understood and more studies are required.

Plants that are grown on BCS showed unexpected, based on the bibliographic database, leaf discoloration symptoms (Figure 1). This was likely due to leaf chlorosis, a physiopathy that is characterized by slight chlorotic speckling and marginal necrosis that initially spreads in older basal leaves and consequently to younger growths [57]. This physiopathy is particularly frequent in geranium due to the pH status of the growth media. The pH level can indeed affect the capability of plants to uptake nutrients, thus leading to nutrient deficiency or toxicity [57–62]. An analysis of the nutrient contents in the leaves of the symptomatic plants (Table 3) indicated a high concentration of Fe and Mn, as compared to those that are found in the leaves cultivated using SDS and CS. This condition can result in leaf discoloration that, by reducing the photosynthetic efficiency, indirectly affects crop growth [63]. Several studies reported that the toxicity can be due to an overload of Fe in different forms: ferrous sulfate, ferrous ammonium sulfate, ferric glucoheptonate, and ferric citrate are recognized to be moderately toxic to zonal geraniums at high application rates [61], while Fe chelates showed high toxicity when applied in liquid fertilizers [59]. Monteiro and Winterbourn [64] indicated that an excess of iron absorption might induce the production of free radicals that can oxidize the chlorophyll, which thus causes a decrease in the chlorophyll content. Arunachalam et al. [65], who reported decreases in the chlorophyll content as a consequence of increasing Fe concentrations, also confirmed this process. Conversely, Lee et al. [60] reported no visible toxicity symptoms regarding zonal geranium growth while using ferrous sulfate.

Figure 1. A non-symptomatic leaf (center) and leaf discoloration in symptomatic plants (lateral).

4.5. Essential Oil Yield and Quality

The observed oil yield decreases using growth media rich in nutrients, as reported by several studies: Ram et al. [18] reported that, in India, an increase of paddy straw mulch and nitrogen rates led to a considerable decrease in the oil yield in *P. graveolens*. Ram and Kumar [66], observed the same phenomenon in menthol mint leaves, which suggested that high nutrient availability can produce an increase in the size of the cell, with a consequent dilution of essential oil. The oil quality in geranium is commercially determined by the citronellol and geraniol ratio (C/G). These two components are known for their existing interconversion, where geraniol is the precursor of citronellol [19]. The range of the C/G ratio between 1 and 3, where the highest quality is found when the ratio is closer to 1, which generally indicates a high-quality product that is acceptable for the perfume industry, whilst oils exceeding this range are considered of low quality and, therefore, are used for the production of creams, toiletry, soaps, etc. [19,67]. In this study, the essential oils that were obtained from all growth media showed a C/G ratio within the range of 1–3, which confirms that, in *P. graveolens*, the use of organic amendments does not change the overall quality [18].

5. Conclusions

Biochar has stimulated great interest in recent years, since it appears to be capable of enhancing sustainable agricultural production and contributing to climate mitigation. In this study, biochar and feedstock (solid digestate) were evaluated as a soil amendment in *P. graveolens*. The results showed that the pyrolysis of solid digestate caused a decrease in the bulk density (−52%) and an increase in both the soil pH (+16%) and electrical conductivity (+9.5%). The best crop performances (number of leaves, number of total branches, and plant dry weight) and the final essential oil content (EOpl) were found while using biochar with respect to solid digestate. On the contrary, the use of three different growth media only slightly influenced the oil quality, leaving their chemical characteristics within the range (C/G ratio of 1–3) that is recommended by the international standard trade for high-quality oils. Finally, most likely due to the high content of Fe and Mn, biochar may have induced the presence of chlorosis in the leaves of *P. graveolens*. This suggests a careful application of biochar to the soil is necessary in order to avoid the risks of nutrient deficiency or toxicity, which may reduce the plant biomass. This research demonstrates that biochar obtained from solid digestate, when applied in *P. graveolens* cultivation, may increase crop performances, in particular, the size of leaves, in terms of essential oil production. However, several conclusive remarks on crop performances in relation to biochar application and fertilization rates are still missing, which thus suggests the need for additional studies on CEC, surface area, and porosity. A more detailed analysis of the relationship between biochar nutrient uptake and the degree of physiopathy is also recommended.

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