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Combining Different Approaches for Grape Pomace Valorization: Polyphenols Extraction and Composting of the Exhausted Biomass

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Abstract: Grape pomace represents 60%, by weight, of the solid side-streams of the wine-making process. The quantities produced, seasonality, and the presence of polyphenols pose economic and environmental issues that require proper management approaches based on the principles of sustainability and circular economy. The present work focuses on the combined application of solid–liquid extraction of polyphenols from ground grape pomace using a hydroethanolic mixture and the composting of the exhausted pomace. The obtained results support the possibility of recovering approximately 76.5 g of extract per kg of dry grape pomace (or 1.8 g of total phenols per kg of dry grape pomace). The composting process was not affected by the extraction process. On the contrary, the composting process was enhanced by the pomace particle size reduction, in terms of final biostability and content of humic acids.

Keywords: Cannonau cultivar; solid-liquid extraction; compost quality; humification index; seedlings; plant growth

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1. Introduction

Grapevine (*Vitis vinifera* L., Vitaceae) is one of the most important fruit crops in the world, with over 60 million tons produced per year, and Italy, France, and Spain are the leading countries [1]. Approximately 60% of the grape fruit is used in the wine industry, also yielding solid side-streams equivalent to approximately 25%, by weight, of the original mass [2]. Grape pomace represents 60%, by weight, of such solid side-streams, resulting from the mechanical pressing of grapes, and consists of seeds, skins, and some parts of the stalks [3,4]. The produced amounts, seasonality, physico-chemical properties, and increasingly strict environmental requirements represent economic and environmental issues that require the development of adequate management approaches based on the principles of sustainability and a circular economy [2,5,6]. In this respect, the significant presence of bioactive molecules, especially polyphenols, is an interesting feature as they are anti-aging, antioxidant, antibacterial, and anti-inflammatory. Therefore, the extraction and recovery of polyphenols from grape pomace may be functional for manufacturing nutraceutical and pharmaceutical products for human health [7–11]. Grape pomace contains other valuable components such as lignocellulosic compounds, lignin,

tannins, fibers, sugars, lipids, nitrogen, and minerals, which are beneficial to soils if added in the form of composted soil improver [12]. Indeed, several compounds found in grape pomace act as growth regulators for many vascular crop plants, stimulating the uptake of mineral macronutrients, e.g., potassium, as previously confirmed for maize, pepper, and trifolium [13].

Efficient, sustainable, and eco-friendly extraction methods can be applied to extract polyphenols without compromising the physico-chemical and biological properties of the exhausted pomace [1,14,15]. Solid–liquid extraction is one of the classical conventional methods applied, which avoids additional dissipative processes and yields interesting results using food-grade solvents [14,16]. Moreover, the solid–liquid extraction can be enhanced by applying preliminary grinding, ultrasound- or microwave-assisted extraction, supercritical fluid extraction, and pressurized liquid extraction to reduce the process duration and temperature [16–23]. On the contrary, these processes improve the extraction yield and time but increase the energy consumption.

Aerobic composting allows one to convert grape pomace into a soil improver capable of restoring the organic carbon and nutrient content in soils and increasing the water-holding capacity [2]. Several studies have been performed on the composting of grape pomace alone or with other residues (sugarcane bagasse, organic fraction of municipal solid waste (MSWOF), manure), as well as on vermicomposting [2,24,25]. Moreover, the composting process can be enhanced using grape stalks as a bulking material to ensure a porosity adequate to the aerobic nature of the treatment [26]. The quality of the final product, in terms of, e.g., C/N (in the range of 32–45, [27]) and the humification index (in terms of the humic-to-fulvic-acids ratio, equal to 0.9, [25]) was reported to be comparable to that obtainable from other organic substrates, but with a higher calcium content due to the winemaking conditions [28]. Composted pomace was proven to foster the physical, chemical, and biological properties of soils [29]. Studies performed by Ferrer et al. (2001) highlighted the positive effects achievable for maize seed germination in greenhouses by using 1–4 ton/ha of compost from pomace [30], and Gaiotti et al. (2016) reported that pomace compost was effective in returning nutrients to vineyard soils [31]. Pomace acidity could be an issue to be eventually addressed through the co-treatment with other substrates (e.g., MSWOF), with mutual benefits as grape pomace mitigates the emission of bad odors and enriches the final product with nitrogen and phosphorus [32].

The management of grape pomace can no longer be based on the direct application of single processes that entail the mineralization of the organic matter or its radical rearrangement (e.g., aerobic composting with the conversion of the organic carbon into CO_2 and humic matter). Conversely, a combination of valorization processes characterized by decreasing selectivity would be more appropriate to avoid compromising the possibility of recovering intact compounds that have a high market value [33]. Consistently, the first phases should include pretreatments and treatments aimed at selectively extracting the molecules of industrial interest, while the closure of the cycle would be ensured by treatments that convert/stabilize the bulk exhausted organic matter. In this framework, the present study focused on the combined application of polyphenols extraction and composting. To this aim, polyphenols extraction was carried out through preliminary particle size reduction followed by a solid–liquid process using a hydroethanolic mixture. The composting of grape pomace was performed at the lab scale after combined particle size reduction and polyphenols extraction, as well as on the raw grape pomace with its original content of polyphenols. The quality of the final composts was evaluated by characterizing the final product and performing seed germination and growth tests.

This approach is in line with the principles of the circular economy, as it optimizes the valorization of grape pomace either quantitatively or qualitatively. From a qualitative point of view, the recovery of high-added-value compounds with global marketability (polyphenols) would support the production of a low-market-value material destined for short-chain use (compost). From a quantitative point of view, the zero-waste goal would be

pursued, recycling the exhausted substrate resulting from the extraction of the polyphenols, and transforming it into a material of certain and direct use in the winery sector.

In this context, the objectives of the experimental activity were (i) the evaluation of the effectiveness of a gentle polyphenol extraction process, (ii) its effects on the possibility of obtaining good-quality compost, and (iii) the assessment of the effects of the original content of polyphenols on the evolution of aerobic stabilization. To the best of the authors' knowledge, there are no studies on such a combination of processes aimed at grape pomace valorization.

2. Materials and Methods

2.1. Feedstock and Reagents

The grape pomace (GP hereafter) considered in the study consists of skins and seeds from winemaking with the Cannonau cultivar and was kindly supplied by Cantine Argiolas (Sardinia, Italy) during the 2019 harvest season. Grape stalks were also collected, manually shredded into 2–5 cm pieces, and used as bulking material for the composting tests. All the solvents and chemicals used in this study were of analytical grade. Ethanol was purchased from Merck (Darmstadt, Germany). Ultrapure water (18 MΩ·cm) was obtained with a Milli-Q Advantage A10 System apparatus (Millipore, Milan, Italy). Folin–Ciocalteu's reagent and sodium carbonate were purchased from Merck, Sigma-Aldrich, Fluka (Milan, Italy).

2.2. Substrates Characterization

Total solids (TS) and volatile solids (VS) were analyzed according to the APHA methods [34]. Carbon and nitrogen were evaluated using a CHN analyzer (LECO, Truspec CHN, St. Joseph, MI, USA). The particle size of the ground pomace was measured with a laser diffraction particle size analyzer (Malvern Mastersizer 3000, Malvern Panalytical Ltd., Worcestershire, UK), by using the wet dispersion method and distilled water as the dispersant. The pH and electrical conductivity values were measured using a pH-meter (Orion4 Star, Thermo Fisher Scientific, Waltham, MA, USA) and a conductivity meter (HQ30d, Hach Company, Ames, CO, USA).

2.3. Extraction Procedure, HPLC-DAD Extract Analysis, Determination of Total Phenolic Content

The pomace was dried at 40 °C for approximately 48 h, ground to obtain a fine powder, and stored under a vacuum and in the dark at 25 °C until use to prevent degradation [35]. The ground pomace (100 g) was suspended in 1 L of a mixture of ethanol and water (70:30 v/v, density 0.885 g/mL), and left under stirring in the dark at 25 °C for 48 h. At the end of the extraction process, the dispersion was centrifuged two times (30 min, 8000 rpm) to separate the solid and liquid fractions [16,36]. The exhausted pomace (solid fraction) was recovered for the composting experiment. The extraction yield (Y_{ext}, % TS) was calculated from the following equation (Equation (1)):

$$Y_{ext}(\%) = \frac{W_1}{W_2} * 100 \quad (1)$$

where W_1 is the dry weight of the extract and W_2 is the dry weight of pomaces.

The extracted phenolic compounds were identified and quantified using an HPLC (Agilent 1260 Infinity II) fitted with a pump module G7111A, an autosampler module G7129A, and an Agilent G4212B photodiode array detector (Agilent Technologies, Cernusco sul Naviglio, MI, Italy) [37]. Separation was obtained with a Kinetex EVO C18 column (150 × 4.60 mm, 2.6 µm, Phenomenex, Casalecchio di Reno, BO, Italy) using 0.22 M phosphoric acid (solvent A) and acetonitrile (solvent B) as the mobile phase, at a constant flow rate of 0.8 mL/min. The gradient (v/v) was generated, decreasing from 100% solvent A to 80% in 20 min, to 70% in 35 min, to 0% in 45 min, and then remaining stable up to 50 min; finally, the gradient reached 100% and was maintained stable for 5 min before injection. Dry extracts were diluted at 1:25 w/v with a mixture of MeOH:H_2O (80:20 v/v) to make them suitable for analytical analysis. The extract solutions were further diluted

1:5 with H_3PO_4 0.22 M. Solutions were filtered with a 0.45 µm CA syringe filter when cloudy. The injection volume was 10 µL. The chromatograms and spectra were elaborated with an OpenLab V. 2.51 data system (Agilent Technologies, Cernusco sul Naviglio, MI, Italy), and polyphenols were detected and quantified according to the main classes: Anthocyanins at 520 nm, flavonols at 360 nm, hydroxycinnamic acids at 313 nm, benzoic acids at 280 nm, and flavan-3-ols and aromatic amino acids at 210 nm. Stock standard solutions were prepared in methanol or ultrapure water. The calibration curves for commercial standards were plotted with the method of the external standard, correlating the peak area with the concentration by the least-squares method, with a coefficient of determination (R^2) > 0.998 in the range of 0.4–40 mg/L for all the compounds. Individual components were identified, or tentatively, by comparing the retention time and UV-VIS spectra of pure commercial standards or the UV-VIS spectra and the chromatographic profile described in the literature [38].

The total phenolic content was determined spectrophotometrically by the Folin–Ciocalteu method with some modification [39]. In each volumetric flask with 500 µL of Folin–Ciocalteu reagent, 100 µL of the diluted extract solution was added. After five min, 3 mL of 10% sodium carbonate (*w*/*v*) was added, and the mixture was manually shaken and diluted with water to a final volume of 10 mL. After 90 min of incubation at room temperature, in the dark, the absorbance was read at 725 nm. The total phenolic content was expressed as mg GAE/g TS using the calibration curve made of freshly prepared gallic acid standard solutions (10–200 mg/L).

2.4. Composting Tests

Composting tests were performed on the grape pomace previously ground and treated to extract polyphenols (post-ext_groundGP hereafter). By way of comparison, the tests were also performed on raw pomace (i.e., no grinding and no polyphenols extraction) (pre-ext_rawGP hereafter) and ground raw pomace (pre-ext_groundGP hereafter). The pomace was mixed with shredded stalks according to a ratio of 70:30 (% *w*/*w*) to ensure adequate free air space. The water content of the mixtures was preliminarily set at 40% by weight by adding tap water and periodically restored during the treatment to avoid inhibiting effects on the activity of microorganisms. The aerobic treatment was carried out in closed PVC reactors (64 L, 39.5 × 56 × 29 cm) provided with a rigid plastic grid at the bottom to collect the process water. The reactors were insulated with 4 cm thick layers of polyurethane foam. During the first 30 days (active composting phase—ACT), oxygen was supplied through forced aeration according to an airflow rate of 50 L_{air}/h kg TS, using a PVC pipe passing through the mixture and provided with 3 mm diameter holes spaced 20 cm apart. The mixtures were also manually turned daily to further promote aeration and homogeneous process conditions. The composting process lasted 90 days (30 days of ACT + 60 days of curing) and was monitored by carrying out periodic determinations of temperature, water and volatile solids content, pH, and electrical conductivity; all the determinations were carried out by randomly taking samples from the mixture mass, which were successively homogenized to obtain a single representative sample of approximately 50 g. Table 1 provides data on the characterization of the three mixtures to be composted.

The temperature was measured during the process by placing a thermocouple at an intermediate depth at five different points: At the corners (T1 to T4) and in the center of the reactor (Tc). The temperature in the room where the reactors were located was periodically monitored as well.

Table 1. Characterization of the three mixtures of pomace and stalks to be composted.

Parameter	Unit	Pre-ext_rawGP [1]	Pre-ext_groundGP [2]	Post-ext_groundGP [3]
Total solids (TS)	[% *w*/*w*]	61.20 ± 1.62	63.30 ± 0.02	63.50 ± 3.52
Volatile solids (VS)	[% TS]	86.20 ± 0.36	89.30 ± 0.08	85.30 ± 1.20
pH	-	3.75 ± 0.09	3.69 ± 0.00	3.76 ± 0.00
Electrical conductivity (EC)	[mS/cm]	1.05 ± 0.00	1.81 ± 0.15	1.56 ± 0.08
Carbon	[% TS]	47.52 ± 0.14	47.52 ± 0.14	48.12 ± 0.15
Nitrogen	[% TS]	1.68 ± 0.12	1.68 ± 0.12	1.72 ± 0.14
Carbon/Nitrogen (C/N)	-	28.20	28.20	27.98
Bulk density (BD)	[kg/m^3]	213	273	265
Particle density (PD)	[kg/m^3]	1214	1208	1198
Free air space (FAS)	[%]	81.0	75.7	76.3
Total phenolic content	[mgGAE/g_{TS}]	4.05 ± 0.14	7.13 ± 0.64	2.73 ± 0.34

Mean values ± standard deviations were reported. [1] Pre-extraction raw grape pomace + stalks; [2] Pre-extraction ground grape pomace + stalks; [3] Post-extraction ground grape pomace + stalks.

Information on the product bio-stability was also obtained by performing the 4-day respiration index test (RI_4) under static conditions and according to the second draft of the Working Document on the Biological Treatment of Biowaste [42–44]; the RI_4 was assessed at the beginning of the test, after 30 days of treatment and after 90 days (i.e., at the end of the process) by using a static automatic electrolytic respirometer (Sapromat, H+P Labortechnik AG, Germany). The static RI_4 was calculated as the cumulative oxygen consumed after four days net of the duration of the lag-phase [43], and the value is given in milligrams of consumed oxygen per grams of total solids (mg O_2/g_{TS}).

Humic matter (*Cext*), fulvic (*FA*), and humic acids (*HA*) were determined according to Roletto et al. (1985) and measured as carbon using a *TOC* analyzer (TOC-VCSN and SSM-5000A, Shimadzu Corporation, Japan) [45]. The humification ratio (*HR*) and the humification index (*HI*) were calculated according to Equations (3) and (4) [45,46]:

$$HR\ (\%) = \frac{Cext}{TOC} \cdot 100 \quad (3)$$

$$HI\ (\%) = \frac{HA}{TOC} \cdot 100 \quad (4)$$

2.5. Seed Germination and Seedling Growth

The quality of the produced compost was evaluated in terms of germination and seedling growth; the test was also performed on compost cured for a further 90 days to evaluate the effects of an intermediate storage period between the end of the process and the application on the soil. The tests were performed using a dicotyledon plant species, the garden cress (*Lepidium sativum* L.), which is an annual, glabrous, erect, and edible herb, a member of the Brassicaceae family. The composts were preliminarily mixed with soil according to different ratios (5, 10, and 15% *w*/*w*); the soil composition consisted of peat (55% *w*/*w*), perlite (35% *w*/*w*), and coconut fiber (10% *w*/*w*). The compost/soil mixture was sterilized in an oven before the tests (five hours at 80 °C). Thirty seeds were placed in a pot containing 250 g of the compost/soil mixture (two replicates for each mixture). Plants were incubated in a phytotron chamber at 25/10 °C with a 12/12 h regime of light and dark. After three weeks of incubation in the phytotron, the percentage of the germination index, the epicotyl height, the total plant height (including roots), the number of leaves, the fresh biomass, and the dry biomass were assessed.

2.6. Statistical Analysis

All the analyses were performed in triplicate, and the results are presented as mean values ± standard deviation. The error bars represent the measurement repeatability calculated as the standard deviation of the mean values. One-way analysis of variance

(ANOVA) was used to compare different composting treatments. Statistical differences among germination and seedling growth means were determined by using analysis of variance (ANOVA) and Dunnett's t-test in comparison [47]. p values < 0.05 were considered significantly different. The results were analyzed using the SPSS-11 software.

3. Results and Discussion

3.1. Polyphenols Extraction

The obtained extract was purple colored, sticky, and highly hygroscopic. As reported in previous studies, Y_{ext} was 7.65 ± 0.46% [36,48], which implies that the bulk of the pomace mass remained available for the composting step. Five different classes of polyphenols (anthocyanins, flavonols, hydroxycinnamic and hydroxybenzoic acids, and flavan-3-ols) were identified in the extracts (Table 2).

Malvidin-3-*O*-glucoside and malvidin-3-*O*-(*p*-coumaroyl)glucoside were the most abundant anthocyanins, while other anthocyanins (e.g., delphinidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, and their derivatives) were detected in lower amounts. If compared with other studies, the detected levels of anthocyanins are significantly lower [49].

Considering flavonols, Fontana et al.'s (2017) values of the considered four different red grape varieties ranged between 0.58 and 1.73 mg/g_{TS}. Similar results were obtained in this study, as the total flavanols were 1.46 mg/g_{TS}, with quercetin (0.45 mg/g_{TS}) and quercetin-3-*O*-glucuronide (0.37 mg/g_{TS}) as the flavonols identified in higher amounts. Vanillic acid (1.18 mg/g_{TS}) was the most abundant phenolic acid detected in the extract, followed by hydroxybenzoic acid, which was detected in a higher amount than hydroxycinnamic acid. Among flavan-3-ols, catechin (2.98 mg/g_{TS}) and (−)-epicatechin (1.77 mg/g_{TS}) were the most abundant. The obtained extract was rich in polyphenols (23.33 mg/g_{TS}), with flavan 3-ols as the one present in greater quantity (11.16 mg/g_{TS}, almost 50% of the total phenolic content); similar results were found by Fontana et al. (2017), who found the highest amount of flavan 3-ols was approximately 12.88 mg/g_{TS} in the Cabernet Sauvignon grape variety [49].

Finally, the total phenolic content of the obtained extract was measured according to the Folin–Ciocalteu method. The Folin–Ciocalteu method confirmed the data obtained with HPLC, as the total phenolic content was 185.1 ± 10.4 mg GAE/g_{TS}. These results are in accordance with those found by Antoniolli et al. (2015), as they detected levels of 196.2 ± 22.7 mg GAE/g_{TS} in Malbec grape pomaces extract [50].

Table 2. Type and amounts of polar compounds found in the extract obtained from the ground Cannonau pomace.

Retention Time [min]	Compound	Id [a]	Content [mg/g_{TS}]
	Total Anthocyanins		**6.12 ± 0.05**
18.66	Malvidin-3-*O*-glucoside	Rt	1.19 ± 0.00
28.40	Malvidin-3-*O*-(*p*-coumaroyl)glucoside [b]	UV-Vis	2.26 ± 0.04
	Other Anthocyanins [b]	UV-Vis	2.67 ± 0.03
	Total Flavonols		**1.46 ± 0.03**
21.95	Quercetin-3-*O*-galactoside	Rt	0.06 ± 0.00
22.08	Quercetin-3-*O*-glucoside	Rt	0.18 ± 0.00
22.25	Quercetin derivative [c]	UV-Vis	0.03 ± 0.00
24.56	Quercetin-3-*O*-glucuronide	Rt	0.37 ± 0.00
29.46	Quercetin	Rt	0.45 ± 0.01
	Other flavonols [c]	UV-Vis	0.36 ± 0.02

Table 2. *Cont.*

Retention Time [min]	Compound	Id [a]	Content [mg/g_{TS}]
	Total Hydroxycinnamic acids		**1.30 ± 0.00**
11.23	Caftaric acid	Rt	0.17 ± 0.00
13.20	Hydroxycinnamic derivative [d]	UV-Vis	0.14 ± 0.00
14.40	*p*-Coumaric acid derivative [d]	UV-Vis	0.11 ± 0.00
15.03	Caffeic acid derivative [d]	UV-Vis	0.14 ± 0.00
16.26	*p*-Coumaric acid	Rt	0.07 ± 0.00
19.31	Hydroxycinnamic derivative [d]	UV-Vis	0.08 ± 0.00
	Other Hydroxycinnamic acids [d]	UV-Vis	0.59 ± 0.03
	Total Hydroxybenzoic acids		**3.30 ± 0.03**
4.91	Gallic acid	Rt	0.61 ± 0.01
7.24	Protocatechuic acid	Rt	0.09 ± 0.00
12.01	Vanillic acid	Rt	1.18 ± 0.01
13.63	Syringic acid	Rt	0.61 ± 0.00
21.49	Ellagic acid	Rt	0.14 ± 0.00
	Other Hydroxybenzoic acids [e]	UV-Vis	0.67 ± 0.01
	Total Flavan 3-ols		**11.16 ± 0.37**
12.18	Procyanidin B1	Rt	1.22 ± 0.16
12.40	(+)-Catechin	Rt	2.98 ± 0.03
14.67	Procyanidin B2 [f]	UV-Vis	1.56 ± 0.11
15.10	(-)-Epicatechin	Rt	1.77 ± 0.04
17.47	Procyanidin B3 [f]	UV-Vis	1.19 ± 0.05
	Other Flavan-3-ols [f]	UV-Vis	2.45 ± 0.19
	Total polyphenols		**23.33 ± 0.48**
	Other compounds		
3.17	Xanthine	Rt	0.49 ± 0.00
4.41	Tyrosine I	Rt	1.20 ± 0.02
5.64	Phenylalanine	Rt	1.19 ± 0.03
9.07	Tyrosine II	Rt	0.10 ± 0.00
9.69	Tryptophan I	Rt	0.76 ± 0.00
13.18	Tryptophan II	Rt	0.33 ± 0.02
15.50	Tryptophan III	Rt	0.08 ± 0.00
	TOTAL		**27.49 ± 0.55**

The results are reported as mean value ± standard deviation (n = 3). [a] Id: Identification: Rt, comparison with retention time and UV-VIS spectra of pure standard; UV-Vis, comparison with UV-VIS spectra of pure compound or similar pure standards and literature data; [b] dosed with the calibration curve of malvidin-3-*O*-glucoside; [c] dosed with the calibration curve of quercetin-3-*O*-glucoside; [d] dosed with the calibration curve of caftaric acid; [e] dosed with the calibration curve of gallic acid; [f] dosed with the calibration curve of procyanidin B1.

3.2. Evolution of the Composting Process and Quality of the Products

3.2.1. Temperature

Considering the strong exothermicity of the aerobic degradation, monitoring the temperature of the mass undergoing the treatment provides reliable information on the evolution of the process. The trend over time of the temperature values is presented in Figure 1. A rapid increase in temperature (the so-called "active phase" or ACT) observed for all three mixtures and the absence of a lag phase suggests a good and ready affinity between the substrate and the typical aerobic microorganisms, actinomycetes, and fungi [51]. No significant differences related to either the preliminary size reduction or the extraction treatment were observed. However, despite the similar trends, the higher temperature values observed for the mixtures containing ground pomace (58–61 °C as compared to 39 °C observed for the mixture containing raw pomace) and the longer thermophilic phase (15 days as compared to 5 days observed for the mixture containing raw pomace), highlight the influence of the particle size. The preliminary size reduction did not limit oxygen

diffusion or segregate the availability of water thanks to the presence of stalks as bulking material but increased the specific reactive surface and possibly limited heat dispersion, as also observed in other studies [6,52,53]. The ground-pomace mixtures are characterized by a slightly lower free air space (FAS = 76% vs. 81%). The free air space is calculated as the ratio between the volume of the pores filled with gas and the total volume and influences the air circulation and removal of heat and moisture [54,55]. A 30% FAS is considered the minimum to guarantee the onset of aerobic conditions in the mass under treatment, but optimal values span between 60 and 85% [3,55]. It is worth mentioning that only the mixtures containing ground pomace reached and maintained the temperature of 55 °C for at least 3 days, as required by Italian legislation to guarantee the sanitation of the material. However, it should not be overlooked that the maximum temperature values also are influenced by the mass to be treated and the size of the windrow [2,56,57]. This is confirmed by the fact that no significant differences were found between the temperature values detected at the various measurement points, which are instead observed in large windrows; on the other hand, the homogeneity of the observed values also supports the correct configuration and management of the laboratory reactors. The thermophilic phase (i.e., active phase, or ACT) lasted approximately 15 days for the mixtures containing the ground pomace, and it was followed by a gradual decrease caused by the slowdown of the microbial activity, which led the observed values to converge towards the ambient temperature (i.e., the maturation phase) [58]. Similar results were observed by [58] who worked on similar substrates. Contrary to what was observed for the size reduction pre-treatment, the preliminary extraction did not entail significant differences in the evolution of the process. Ultimately, the microorganisms involved in the composting process proved to be able to deal with the initial phenol content without negative effects as also observed by Santos et al. [57], instead being more influenced by process conditions such as the particle size of the pomace [59].

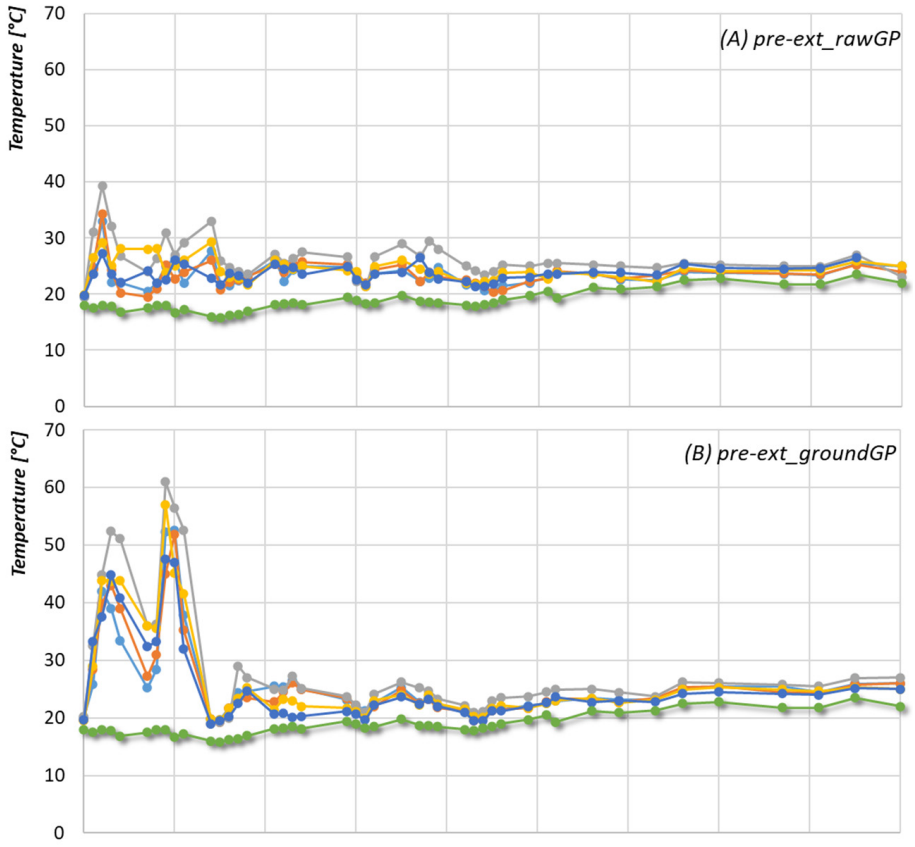

Figure 1. *Cont.*

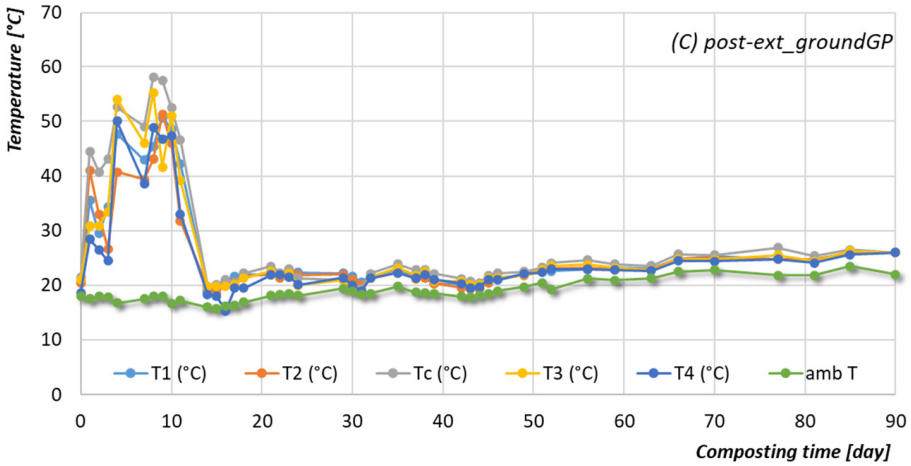

Figure 1. Grape pomace composting—evolution over time of the temperature values measured at the corners (T1–T4) and in the center (Tc) of the composting reactors; (**A**) pre-extraction not-ground grape pomace (pre-ext_rawGP); (**B**) pre-extraction ground grape pomace (pre-ext_groundGP); (**C**) post-extraction ground grape pomace (post-ext_groundGP).

3.2.2. pH and Electrical Conductivity

Figure 2 presents the trends for the pH and electrical conductivity values assessed for the three pomace/stalks mixtures. For all three mixtures, the pH values fell within an initial narrow range (3.69–3.76) and showed an increasing trend up to a plateau in the alkaline range (9.7–10.1), reached at the end of the active aerobic phase as typically observed in composting processes [60]. However, in a similar way to what was observed for the temperature values, the pH of the raw grape pomace is characterized by a longer period in the acid range (17 vs. 10 days, for raw and ground pomace, respectively, Figure 2). Therefore, it seems to be confirmed that the raw GP represents a slightly more difficult substrate for microorganisms, although the biomass proved to be able to bring the pH towards the optimal range 6–8 reported by Fernandez et al. (2008), thanks to the breakdown of acidic compounds, such as carboxylic and phenolic groups, and the degradation of proteins and peptides to form ammonia [61,62].

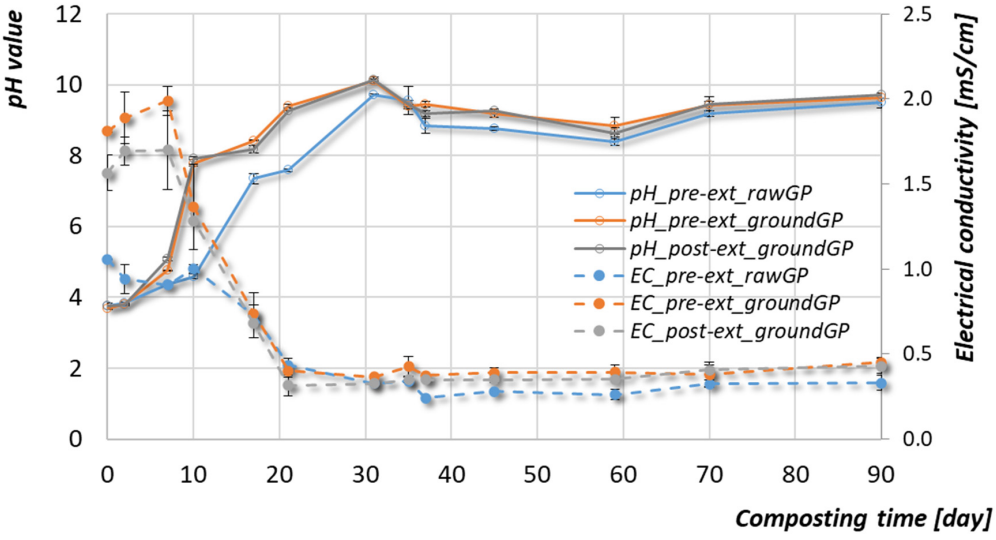

Figure 2. Grape pomace composting—evolution over time of pH (solid line) and electrical conductivity (dotted line) for the three mixtures; pre-extraction not-ground grape pomace (pre-ext_rawGP); pre-extraction ground grape pomace (pre-ext_groundGP); post-extraction ground grape pomace (post-ext_groundGP).

Further confirmation of the differences induced in the process by the preliminary size reduction, but not by the extraction, comes from the EC values. At the beginning of the aerobic treatment, the electrical conductivity of the ground pomace was higher than for the raw pomace (1.6–1.8 mS/cm vs. 1.1 mS/cm), but this difference is no longer significant after the 17th day. The initial difference was likely due to grinding and the resulting high specific surface that fostered the release of soluble ionic compounds. The decreasing trend is comparable to what was observed by Paradelo et al. (2013) who worked on similar substrates [52]. The final EC values were slightly lower than 2.0 mS/cm (see Table 3), and fully compatible with the agronomic use according to Gil et al. (2008) who reported an upper limit of 2.5 mS/cm [63].

Table 3. Final characterization of the three composts.

Parameter	Unit	Pre-ext_rawGP [1]	Pre-ext_groundGP [2]	Post-ext_groundGP [3]
Total solids (TS)	[% *w*/*w*]	51.20 ± 1.72	49.70 ± 1.22	50.60 ± 1.32
Volatile solids (VS)	[%TS]	70.86 ± 1.06	69.74 ± 1.38	66.32 ± 1.23
pH	-	9.51 ± 0.09	9.65 ± 0.00	9.71 ± 0.00
Electrical conductivity (EC)	[mS/cm]	0.33 ± 0.03	0.45 ± 0.17	0.43 ± 0.05
Carbon	[%TS]	45.08 ± 1.03	44.68 ± 0.31	44.69 ± 0.06
Nitrogen	[%TS]	2.89 ± 0.28	2.63 ± 0.11	2.64 ± 0.16
Carbon/Nitrogen (C/N)	-	15.59	16.98	16.94
Total phenolic content	[mg GAE/g_{TS}]	2.08 ± 0.66	1.65 ± 0.76	1.61 ± 0.20
Respirometric index (RI4)	[mg O_2/g_{TS}]	11.03 ± 3.64	9.15 ± 0.51	7.13 ± 1.71
Humic acids (HA)	[%TS]	<D.L.	1.50 ± 0.10	1.89 ± 0.20
Fulvic acids (FA)	[%TS]	5.01 ± 0.10	3.86 ± 0.18	2.37 ± 0.19
Humification ratio (HR)	[%TOC]	40.88	50.28	38.96
Humification index (HI)	[%]	-	3.35	4.22

<D.L. = below detection limit. [1] Pre-extraction raw grape pomace + stalks; [2] Pre-extraction ground grape pomace + stalks; [3] Post-extraction ground grape pomace + stalks.

3.2.3. Organic Matter and Phenolic Compounds

Table 3 summarizes the characterization of the produced compost. The evolution over time of the volatile solids content (Figure 3) and respirometric index RI_4 (Figure 4) confirm what was already highlighted by other monitoring parameters, i.e., no significant differences between the treated mixtures, in particular during the first 20 days of treatment, with slightly more pronounced VS removal for the ground and extracted pomace (post-ext_groundGP) during the final stages of the process and ascribable more to the particle size reduction than to the removal of phenols. During the 90 days of treatment, the volatile solids content underwent a reduction from initial values spanning within the range of 85–90% to values falling between 66 and 70%. This relatively limited VS removal is due to the nature of the grape pomace, a fibrous and lignin-rich vegetal substrate [52] as compared to more readily degradable substrates such as, for instance, the organic fractions of municipal solid waste.

The respirometric index RI_4 was assessed for the three mixtures at the beginning of the composting treatment, after 30 days (end of the active phase), and after 90 days (end of the curing phase). The results are consistent with the process that was slower for the raw pomace (Figure 4). The values decreased from the initial ones equal to 30.75 ± 2.31 mg O_2/gTS (pre-ext_rawGP), 31.71 ± 2.24 mg O_2/gTS (pre-ext_groundGP), and 30.62 ± 1.92 mg O_2/gTS (post-ext_groundGP), to 29.00 ± 0.44 mg O_2/gTS (pre-ext_rawGP), 21.11 ± 2.55 mg O_2/gTS (pre-ext_groundGP), and 22.81 ± 2.79 mg O_2/gTS (post-ext_groundGP) after 30 days, and finally to 11.03 ± 3.64 mg O_2/gTS (pre-ext_rawGP), 9.15 ± 0.51 mg O_2/gTS (pre-ext_groundGP), and 7.13 ± 1.71 mg O_2/gTS (post-ext_groundGP) (see Table 3). It is interesting to note how the slower degradability of the raw pomace (pre-ext_rawGP) prevented reaching the limit value for the Static Respiration Index (10 mg O_2/g_{TS}) that is considered indicative of achieved biochemical stability for compost [44].

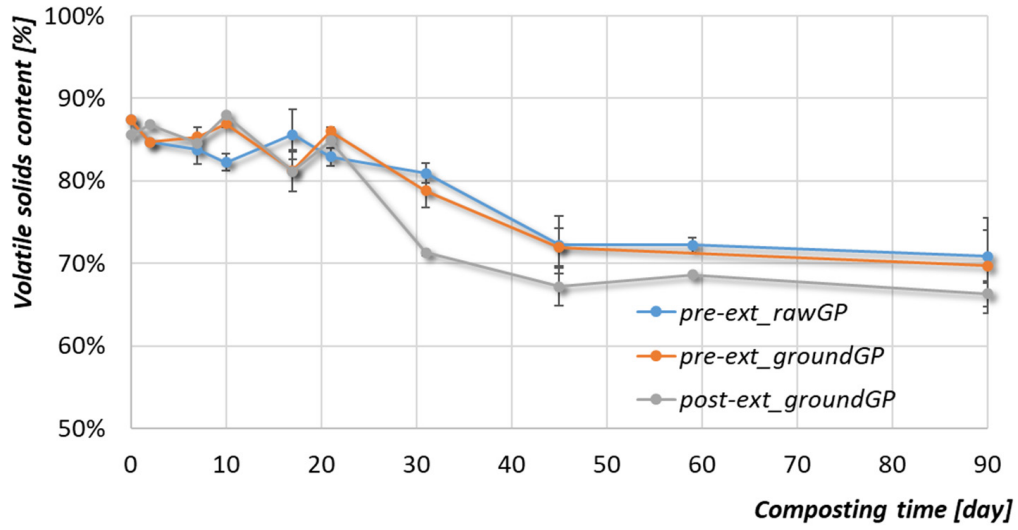

Figure 3. Grape pomace composting—evolution over time of pH (solid line) and electrical conductivity (dotted line) for the three mixtures; pre-extraction not-ground grape pomace (pre-ext_rawGP); pre-extraction ground grape pomace (pre-ext_groundGP); post-extraction ground grape pomace (post-ext_groundGP).

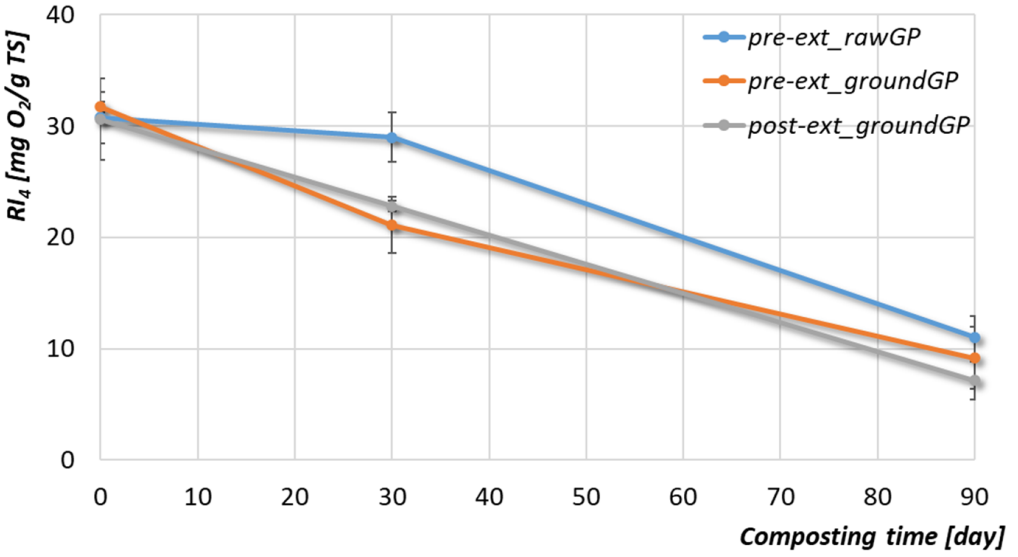

Figure 4. Grape pomace composting—evolution over time of the static respirometric index RI_4 for the three mixtures; pre-extraction not-ground grape pomace (pre-ext_rawGP); pre-extraction ground grape pomace (pre-ext_groundGP); post-extraction ground grape pomace (post-ext_groundGP).

The C/N ratio was found to be approximately 28 for all the mixtures. As expected, it decreased during the composting treatment due to the loss of C [27,52], and for all the mixtures, it reached values below 20, which is considered indicative of having achieved biostability for compost [57,64].

The initial phenolic content of biomasses containing pre-extraction not-ground pomace was 4.05 mg/g_{TS}, for biomasses containing pre-extraction ground pomace it was 7.13 mg/g_{TS}, and for biomasses containing post-extraction ground pomace it was 2.73 mg/g TS (Figure 5). This significant difference in the initial phenolic content between pre-extraction not-ground pomace and pre-extraction ground pomace is due to the particle size, since the reduction in particle size increases the specific surface exposed to the solvent thus enhancing the extraction of polyphenols [65–67].

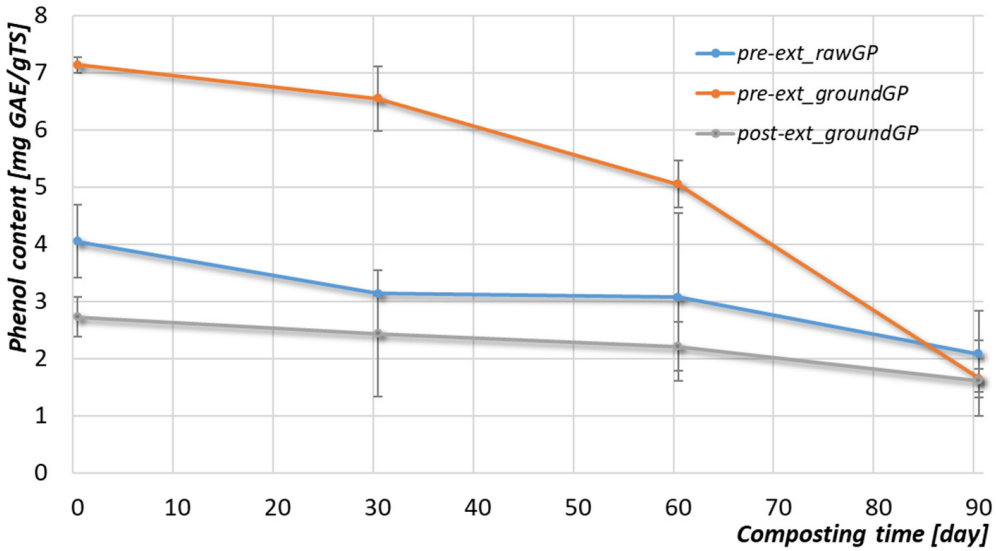

Figure 5. Grape pomace composting—evolution over time of the phenolic content for the three mixtures; pre-extraction not-ground grape pomace (pre-ext_rawGP); pre-extraction ground grape pomace (pre-ext_groundGP); post-extraction ground grape pomace (post-ext_groundGP).

The total phenolic content decreased over time, likely because the polyphenols were incorporated into biosynthetic pathways leading to the formation of humic molecules [68]. The extraction of polyphenols affected the humification ratio (HR), which resulted in being higher for the pre-extraction ground pomace (50.28%) with respect to the post-extraction ground pomace (38.96%). This figure suggests that the presence of polyphenols in the pomace is compatible with composting and could provide precursors for the overall humification process. On the other hand, as far as the speciation of the humic matter in terms of fulvic and humic acids is concerned, the combination of grinding and phenols extraction seems to enhance the production of humic acids (HI% = 4.2%) as compared to grinding alone (3.3%) and, most of all, raw pomace; for raw pomace, it could be the result of the slower and less complete composting process.

3.2.4. Effects on Seed Germination and Seedling Growth

The results of germination and seedling growth tests are summarized in Figure 6. The studied parameters of garden cress (*L. sativum*) as a function of the duration of compost curing were not significantly different ($p > 0.05$). These results are in line with those previously obtained by Martínez Salgado et al. [25], who detected non-statistically significant differences with respect to the duration of compost curing, likely due to the similar humification process and high content of nitrogen.

On the contrary, the pomace treatment affected the plant growth parameters; indeed, compost produced with pre-extraction not-ground pomace (pre-ext rawGP) improved the measured parameters of seedling growth compared to those obtained using other composts produced with ground pomace. The reason might be that not-ground pomace permitted an increment of the oxygen supply to microorganisms and a better homogenization and homogenous distribution of the materials, microorganisms, moisture, and nutrients [28,69].

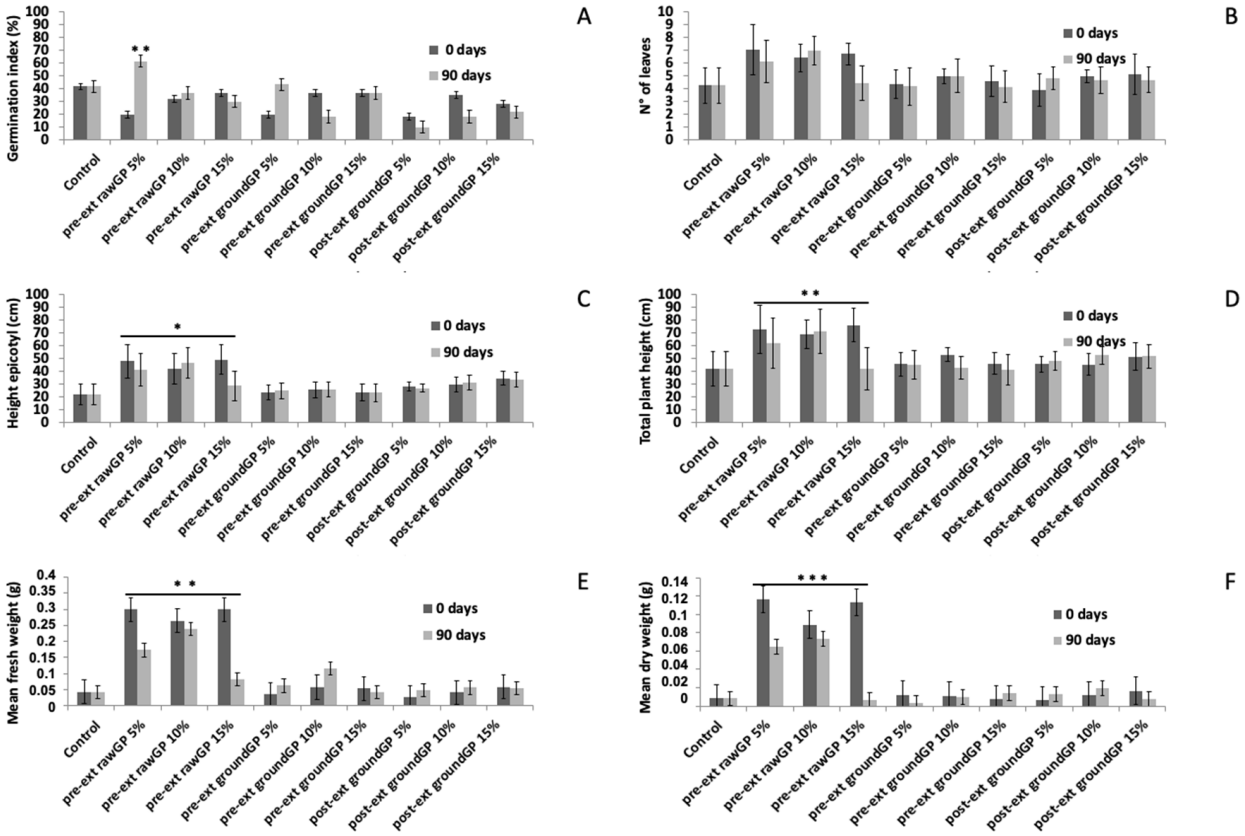

Figure 6. Grape pomace composting—mean values of germination index (**A**), number of leaves (**B**), epicotyl height (**C**), total plant height (**D**), fresh biomass (**E**), and dry biomass (**F**) of *Lepidium sativum* grown in soil improved with 5, 10, and 15% of compost obtained from pre-extraction not-ground pomace (pre-ext rawGP), pre-extraction ground pomace (pre-ext_groundGP), and post-extraction ground pomace (post-ext_groundGP); the compost was tested at the end of the composting process (30 + 60 days), and after a further temporary pre-use storage period of additional 90 days. Values that significantly differ: * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$.

In particular, a higher germination index of plants ($p < 0.05$) was obtained using pre-ext rawGP 5%, with an additional 90 days of curing. An increment of the germination index values of grown garden cress seeds on the grape biodegraded materials was also previously demonstrated by Pinter et al. (2019) [24]. A previous study on the polyphenolic content of grape extract disclosed their influence on the activity of enzymes regulating the carbohydrate metabolism, which positively affected the germination process in general, but whose major action was mainly related to a-amylase activity in the first 24 h of the germination process [70]. Higher epicotyl height ($p < 0.05$) was observed in plants treated with pre-ext _rawGP 5% and 10%, with and without the additional 90 days of curing, and pre-ext_rawGP 15% with an additional 90 days of curing. The total plant height was also higher ($p < 0.01$) when they were grown with pre-ext_rawGP 5% and 10%, with and without an additional 90 days of curing, and pre-ext_rawGP 15% with an additional 90 days of curing $p < 0.050$. These effects could be related to the degradation of organic matter and mineralization that lead to alkaline pH due to the presence of ions, as confirmed by the electrical conductivity confirmed, thus influencing the crop's growth [25]. Considering the number of leaves, no significant differences among compost preparation types were found ($p = 0.058$). Any significant differences ($p < 0.01$ for the fresh biomass and $p < 0.001$ for dry biomass) were found in fresh and dry biomass of plants treated with pre-ext_rawGP 5%, pre-ext_rawGP 10%, and pre-ext_rawGP 15%. The ground or raw state of pomace seems to be a key parameter in plant growth irrespective of the presence of polyphenols [70–72].

In this sense, more detailed experimental studies are needed to reach a better structure of the compost and to increase the quality, including the extraction, to reach the maximum performance of the circular economy of grape processing.

4. Conclusions

The study aims at contributing to the development of integrated processes for the valorization of grape pomace, the main solid side-stream resulting from winemaking.

The results attained support the possibility of combining the recovery of an extract rich in polyphenols, thus characterized by a high market value, and of a soil improver to be used in the agro-industrial sector.

An eco-friendly extraction process was adopted to avoid compromising the physico-chemical and biological properties of the pomace. The composting treatment proved to be feasible for both the raw pomace and the pomace that underwent size reduction or size reduction plus the extraction of polyphenols. It should be emphasized that the composting process was enhanced by the reduction in the pomace particle size, which improved the speed and intensity of the aerobic process with repercussions on some qualitative parameters such as the compost's final biostability and the content of humic acids (*HI*, humification index). On the contrary, the composting process was not significantly affected by either the initial content of polyphenols, which could indeed provide precursors for the overall humification (*HR*, humification ratio), or by the achieved polyphenol extraction. Therefore, the presence of polyphenols in the pomace appears to be compatible with both the direct implementation of composting or with a more complex approach that involves the extraction of valuable compounds followed by composting.

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