Vol.67: e24230183, 2024
https://doi.org/10.1590/1678-4324-2024230183
ISSN 1678-4324 Online Edition

BABT
Brazilian Archives of Biology and Technology

Article - Engineering, Technology and Techniques

Valorization of Wastes Generated in Organic Grape Processing

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Editor-in-Chief: Alexandre Rasi Aoki
Associate Editor: Ana Cláudia Barana

Received: 24-02-2023; Accepted: 18-Oct-2023

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HIGHLIGHTS

- Up to a third of the grape produced for processing is discarded as waste, without valorization.
- Wastes of grape processing are rich in compounds with biological activity.
- This kind of waste is also rich in nutrients making it useful for plant fertilization.
- Wastes from grape processing have the potential to be reused in applications with more added value.

Abstract: The development potential of byproducts from wastes of grape processing can be a promising alternative due to environmental questions. Moreover, there is the possibility of using this material in the development of products with added value. In this study, the wastes of grape skin (GSk), grape seed (GSe), and defatted grape seed with skin fragments (DGS) from 'Ives noir' grape (*Vitis labrusca* L.), grown under organic farming conditions, had their chemical composition and physical-chemical properties evaluated. Parameters of chemical composition, contents of phenolic compounds, total anthocyanins, flavonoids, and minerals, the antioxidant capacity, and water sorption capacity were evaluated. The wastes of grape were also analyzed by FTIR and TG/DTG. All residues had a high fiber content (54.1 – 74.3 wt.%), the DGS waste had the highest contents of phenolic compounds as flavonoids, and the GSk waste had the highest content of total anthocyanins. Antioxidant capacity values were higher in the $ABTS^{+}$ method, with no statistical difference. On the other hand, in the DPPH antioxidant assay, the DGS and GSe wastes had higher antioxidant activity; these wastes also had greater thermal stability. The GSk waste had the highest water sorption capacity. The results show that the wastes from grape processing have the potential to be reused in applications with more value added.

Keywords: Agricultural waste; antioxidant capacity; chemical composition; 'Ives noir' grape; phenolic compounds.

INTRODUCTION

Worldwide grape production in 2020 was 78.03 million tonnes, considering grapes for both processing and in natura consumption. That same year, Brazilian production was 1.43 million tonnes [1]. According to data from the Brazilian Institute of Wine (IBRAVIN) [2], 88.5 % of the national production corresponded to American and hybrid varieties (*Vitis labrusca*), used as a feedstock in the production of juices, wines, and grape derivatives. The remaining 11.5 % were composed of European varieties (*Vitis vinifera*) used in the production of fine wines. In the Rio Grande do Sul state, a major viticultural center in Brazil, the production of grapes destined for the elaboration of wines, sparkling wines, and juices represents about 90 % of the Brazilian production.

Among the many grape cultivars, the 'Ives noir' (*Vitis labrusca*) is widely cultivated in Brazil due to the intense red-violet color, having large amounts of phenolic compounds, such as anthocyanins, which results in the production of wines and juices with sensory and nutraceutical properties that please the consumer market. In addition, this variety has a good performance and resistance to fungal diseases [3-4].

The main solid waste generated in grape processing to obtain wines and juices is the grape marc, resulting from the grape pressing process and composed of grape stalks, skin, residual pulp, and seed. The amount of waste generated depends on the grape variety and the process conditions, but waste yields about 20 – 30 wt.% of the original grape mass. Considering that approximately 750 mL of juice or wine are produced with 1 kg of processed grapes [5-6], there is an estimated annual worldwide production of 8.49 million tonnes of grape marc from grape processing [7]. Considering Brazilian production in the same year and the quantity used in processing, a grape marc amount in the range of 260 – 400 thousand tons that needs some treatment and disposal is generated.

In general, the wastes of grape processing are destined for composting or animal feeding [8]. However, there are some restrictions to these applications, such as the presence of some polyphenols and derivatives, which have antimicrobial activity, hampering the composting process. In addition, some animal species have an intolerance to some compounds present in the waste, such as tannins, hindering the digestibility of this material and limiting its use as a component of animal feeding [9]. Another potential issue is the seasonality of this waste, considering that this waste would be generated in large amounts in a short period, during and immediately after the grape harvest, which, in Brazil, occurs between December and March. The inadequate disposal of this material in the soil is also detrimental. It can cause water tables and soil contamination, impermeabilization issues (due to residual oil in the seed), and insect and fungi proliferation.

The byproducts of wine production and agricultural wastes from plant sources attract considerable attention as potential sources of bioactive compounds, which can be used in several kinds of applications in the food, cosmetics, pharmaceutical, and chemical industries [10-11].

Grape seed is an important component of grape marc, and it has bioactive compounds of industrial interest, such as fatty acids, polyphenols, and E vitamins. The grape seed oil has a high market value due to the presence of polyunsaturated fatty acids [12]. Thus, the waste generated in the processing of grape seeds may be useful to be used in products with uses in the areas of agriculture, food, cosmetics, and pharmaceuticals [13]. For example, grape seed waste may be used as a component of organic fertilizers to enhance soil fertility by composting, being a strategy of direct waste application [14].

The transformation of grape marc into new products with added value contributes to the reduction of the volume of wastes, reducing costs, diversifying the production, and reducing the environmental impacts caused by viticultural activity. It is of importance the knowledge of its main physical-chemical and biological properties for the development of studies to widen the reuse alternatives of this material in different areas, such as food, pharmaceutical industries, cosmetics, and packaging.

It is also worth commenting that there are few studies addressing the characterization of segregated wastes of Ives noir grapes grown under organic farming management from the production of grape juice by the Welch method, and the production of grapeseed oil by cold pressing. The difference lies in the study of the grape skin wastes, grape seed waste, and defatted grape seed with skin fragments and their characterization.

Also noteworthy is the residue from grape juice processing or white grape winemaking. It is a marc not fermented and potentially richer in sugars and phenolic compared to the marc from winemaking. The contact of the skin and seed with fermentation must can bring partial and gradual leaching of phenolic to liquid phase [15].

The variability among the grape varieties and the different effects of each production process of wines and juices cause variations in the composition of the marc and their main components: seeds and skins. In addition, it is important to observe that the marc from red wine production is a fermented byproduct which, in general, does not undergo thermal treatments while the marc from juice production is not fermented, and undergo thermal treatments and enzymatic processes when produced by the Welch method [16].

Given that the wastes of grape processing normally do not generate any profit, the objective of the present work was to characterize different wastes of the processing of organic 'Ives noir' grapes and the production of grape seed oil regarding the chemical composition, contents of minerals, bioactive compounds, water sorption capacity and thermal properties. From the results obtained, potential uses for these wastes will be indicated to give these materials a more sustainable destination and add value to this type of material.

MATERIAL AND METHODS

Obtainment of the wastes from organic grape processing

The wastes from the processing of organic 'Ives noir' grape (*Vitis labrusca* L.) were collected in March 2018, from the company Econatura Produtos Ecológicos e Naturais Ltda (Garibaldi, Brazil). The grape skin (GSk) and grape seed (GSe) were obtained already sorted and dried at 70±2 °C for 12 h. The waste from the cold pressing of grape seed was obtained already dried (70±2 °C for 12 h) and milled, being composed of defatted seeds and skin fragments (DGS).

After collection, the GSk and GSe wastes were manually separated to obtain samples with no other plant material. After, the samples were milled in a knife mill and sieved with a mesh/Tyler 9 sieve (2.0 mm). The pre-treated samples were stored in polyethylene packages and kept away from sunlight at room temperature (15 – 25 °C) until characterization.

A flowchart explaining the generation of the wastes and their pre-treatment before characterization is presented in Figure 1.

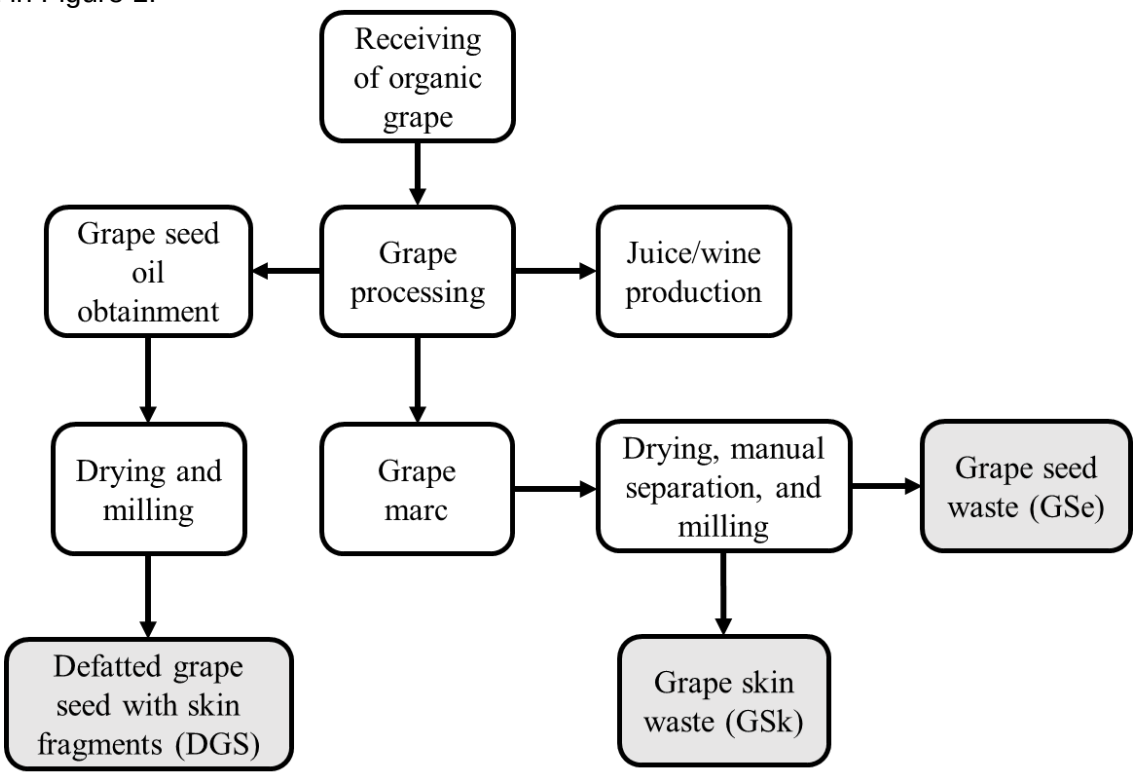

Figure 1. Flowchart of waste generation and pre-treatment steps before characterization.

Chemical characterization and determination of the physical-chemical properties of the wastes

The immediate analysis (determination of ash, lipid, moisture, and volatile material contents) was carried out following the methods described by Institute Adolfo Lutz [17]. Total dietary fiber was determined by enzymatic digestion and gravimetry, following the 991.43 method [18]. Total nitrogen and protein contents were determined with the 991.20 method [19]. Lignin content ('Klason' lignin) was determined under the Tappi T222 om-22 method [20]. Cellulose and hemicellulose contents were determined following the Van Soest

method as described by Silva and Queiroz [21]. Carbohydrate content was determined by mass balance, as recommended by the Brazilian Health Regulatory Agency (ANVISA) resolution RDC n° 360, of December 23, 2013 [22].

Extractives content was determined following the Technical Association of the Pulp and Paper Industry (TAPPI) T 204 cm-97 standard [23], using an ethanol/benzene (1:2 vol.) extracting solution and a glass Soxhlet apparatus with a capacity of 300 mL. The extraction time was 5 h, using 30 g of sample. After extraction, the samples were dried in an oven at 100 °C for 24 h, cooled in a desiccator, and weighed after reaching room temperature. Titratable acidity was determined by the 935.57 method [24]. The contents of macro and micronutrients were determined following the procedures described by Malavolta and coauthors [25].

Determination of total phenolic compounds, flavonoids, and anthocyanins contents

In the determination of the contents of phenolic compounds, flavonoids, and anthocyanins, an extraction procedure was carried out using a hydroalcoholic solution (70 % vol. ethanol). Fifteen grams of sample were put in a 125 mL Erlenmeyer, 50 mL of the hydroalcoholic solution were added, the mixture was left to stand for 24 h at 20±2 °C and protected from light. The supernatant was collected and used in the determination of phenolic compounds, flavonoids, anthocyanins, and the individual contents of phenolic compounds by high-performance liquid chromatography (HPLC).

The content of total phenolic compounds was determined using the Folin-Ciocalteu method [26-27], and the results were expressed as milligrams-equivalent of gallic acid per 100 g of sample. Flavonoid content was determined by the aluminum chloride method, following the procedures of Matic and coauthors [28], and the results were expressed as milligrams-equivalent of quercetin per 100 g of sample. Total anthocyanins content was determined with the differential pH method as described in the Association of Official Agricultural Chemists (AOAC) 2005.02 method [29], and the results were expressed as milligrams-equivalent of cyanidin-3-glycoside per 100 g of sample.

Determination of phenolic compounds by high-performance liquid chromatography (HPLC)

The determination of the content of phenolic compounds was carried out by HPLC, following the procedures described by Morelli and Prado [30]. The extract prepared for the determination of phenolic compounds and anthocyanins was filtered using nylon membranes with a pore size of 0.45 µm. The chromatographic analyses were performed using an HP model 1100 liquid chromatograph (Hewlett-Packard, USA), equipped with a Lichrospher RP18 (5 µm) column and a UV detector in the wavelength of 210 nm.

The following phenolic compounds were evaluated: gallic acid, epigallocatechin, catechin, chlorogenic acid, epigallocatechin gallate, rutin, vitexin, ferulic acid, naringin, hesperidin, resveratrol, quercetin, apigenin, and kaempferol. All standards were dissolved in methanol and used in the external standardization. The reverse-phase analysis was composed of solvent A (Milli-Q water with 1 % v/v phosphoric acid) and solvent B (acetonitrile). The solvent gradient program was 90 % solvent A from zero to 5 min, 60 % solvent A from 5 min to 40 min, and 90 % solvent A from 45 min to 50 min. Mobile phase flow rate was 0.5 $mL \cdot min^{-1}$. The results were expressed as milligrams of substance per kilogram of sample ($mg \cdot kg^{-1}$).

Determination of the antioxidant activity of the wastes

The determination of the antioxidant activity through the neutralization of DPPH radical followed the procedures described by Yamaguchi and coauthors [31], whereas the determination of the antioxidant activity through the neutralization of $ABTS^+$ radical was carried out by the method proposed by Rufino and coauthors [32]. A 5 mL sample of the same hydroalcoholic extract used in the determination of phenolic compounds and total anthocyanins was used in the antioxidant activity tests.

Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG/DTG)

The FTIR analyses were carried out using a Nicolet IS10 infrared spectrophotometer (Thermo Scientific, USA). Each spectrum was obtained with 32 sweeps in the wavenumber range of 400 – 4000 cm^{-1} and a resolution of 0.25 cm^{-1}, in the attenuated total reflection (ATR) mode. The equipment was calibrated before the analysis following the procedures described by the equipment manufacturer.

The TG/DTG tests were done using a TGA-50 thermobalance (Shimadzu, Japan), under an inert gas atmosphere (N_2) with a flow rate of 50 $mL \cdot min^{-1}$. A heating rate of 10 $°C \cdot min^{-1}$ was used, from room temperature (25 °C) up to 900 °C. The mass of each sample was approximately 10 mg, put into silicon carbide

(SiC) crucibles. The thermogravimetry derivative (DTG) curve was generated by the software of the equipment.

Water sorption capacity analysis

The water sorption capacity of the wastes was determined following the method proposed by Vázquez-Ovando and coauthors [33], with modifications. Approximately 2 g of each sample were put in a beaker with 10 mL of distilled water, and the mixture was stirred for 5 min in a magnetic stirrer at 60 rpm. After, the samples were centrifuged at 5,000 rpm for 10 min using a Sigma centrifuge, model 2-16k. The supernatant was discarded, and the wet solid material was weighed to determine the water sorption capacity of the samples.

Experimental design and statistical analysis

The experimental design was completely randomized, being the analyzed factor the type of waste. All analyses were carried out in triplicate. The statistical analyses were done using the Statistical Package for the Social Sciences (SPSS), version 21.0 (IBM, USA). Data normality was verified using Kolmogorov-Smirnov test. The results underwent Analysis of Variance (ANOVA), followed by Tukey's multiple range test at 5 % error probability ($p = 0.05$).

RESULTS AND DISCUSSION

Chemical composition and physical-chemical properties of the wastes

The obtained results regarding the chemical composition and some physical-chemical properties of the studied wastes are presented in Table 1.

Table 1. Chemical composition (in wet basis) and physical-chemical properties of the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS).

Parameter (wt.%)	GSk	GSe	DGS
Moisture	8.52±0.08^a	2.32±0.11^b	2.80±0.05^c
Ash	3.38±0.03^a	1.82±0.02^b	2.15±0.02^c
Lipids	4.63±0.6^a	12.1±0.1^b	6.69±0.25^c
Proteins	10.5±0.1^a	2.74±0.03^b	8.80±0.13^c
Extractives (1)	36.6±0.9^a	20.1±1.5^b	13.2±1.0^c
Carbohydrates (2)	18.9±0.1^a	8.38±3.1^b	5.19±1.46^b
Dietary fiber	54.1±0.6^a	72.6±2.9^b	74.3±1.0^b
Insoluble fiber (3)	51.7±1.5^a	63.7±1.6^b	67.1±1.2^c
Cellulose	14.7±2.2^a	17.6±1.9^b	23.6±1.7^c
Hemicellulose	20.2±0.6^a	11.4±1.4^b	12.0±1.0^b
Lignin	16.8±1.6^a	34.7±1.5^b	31.5±1.0^b
Titratable acidity (4)	4.21±0.16^a	0.28±0.02^b	0.63±0.01^c
pH	3.48±0.02^a	4.74±0.05^b	5.41±0.09^c

(1) Extractives in ethanol/benzene (1:2 vol.) solution. (2) Carbohydrates were determined by difference. (3) Insoluble fiber corresponded to the sum of cellulose, hemicellulose, and lignin contents. (4) Titratable acidity was expressed as gram-equivalents of tartaric acid per 100 g of sample. GSk - grape skin; GSe - grape seed; DGS - defatted seed grape with skin fragments. Means in row followed by the same superscript letter do not differ statistically by Tukey's multiple range test at 5 % error probability ($p < 0.05$).

The results show that the analyzed wastes have high amounts of dietary fiber, in which the GSe and DGS wastes had the highest contents, with no statistical difference between them. According to Prado and coauthors [34], after oil extraction, the remaining grape seed waste is composed mainly of lignin and hemicellulose. These authors, carrying out the characterization of grape seed waste from a winery in Santa Catarina state (South Brazil), reported a lignin content of 46 wt.% in this waste.

Relative to lipid content, the GSe waste had the highest content (12.1 wt.%), while the GSk waste had the lowest one (4.6 wt.%). The DGS waste, even after oil extraction, had a remaining lipid content of 6.7 wt.%. According to García-Lomillo and González-SanJosé [16], grape seed has, in general, lipid contents in the range of 10 – 17 wt.%. The presence of lipids in the waste may indicate the potential use as a source of grapessed oil. In addition, high lipid content may hinder some applications for this waste, especially regarding to rancidity and other oxidation processes.

The GSk waste had the highest moisture, ash, protein, carbohydrates, and extractives contents. Since no fermentation occurs in grape juice production, the skins have higher residual sugar contents, a behavior observed in the present work. Postingher and coauthors [35], producing and characterizing grape marc flour from organic 'Ives noir' grapes (2015 harvest), reported the following results: 21.6 wt.% carbohydrates, 9.4 wt.% proteins, 7.4 wt.% lipids, 47.2 wt.% total fiber, 3.6 wt.% ash, and 10.8 wt.% moisture.

Deng and Zhao [36], reported that waste from grape skins had total dietary fibers of 56.3 wt.%, being most of this fiber classified as insoluble. In addition, protein contents varied between 5.4 and 12.3 wt.%, ash varied between 2.5 and 7.6 wt.%, and the soluble sugar contents varied between 1.3 and 78.0 wt.%. The authors also commented that the wastes from grape skins are an excellent source of dietary fibers rich in bioactive compounds.

Bender and coauthors [37] reported, for the flour of 'Marselan (*V. vinifera*) grape skins, 17.6 wt.% carbohydrates, 6.8 wt.% protein, 5.1 wt.% total fats, 58.0 wt.% total fibers, 12.5 wt.% ash, and 7.2 wt.% moisture. Karnopp and coauthors [38], characterizing the flour of organic 'Ives noir' grape marc (2013 harvest) after seed oil extraction, observed the following composition: 8.6 wt.% moisture, 5.4 wt.% ash, 11.4 wt.% proteins, 7.7 wt.% lipids, and 63.9 wt.% total fibers, from which 55.8 wt.% were non-soluble fiber, and 8.0 wt.% were soluble fiber. Regarding the flour from organic grape skin, the same authors reported 2.4 wt.% moisture, 3.9 wt.% ash, 9.8 wt.% proteins, 8.5 wt.% lipids, and 54.8 wt.% of total fiber, from which 51.0 wt.% were insoluble fiber and 3.8 wt.% were soluble fiber.

Gauer and coauthors [39] reported the following composition for the flour obtained from organic 'Ives noir' grape seeds cold pressed from the 2017 harvest: 6.7 wt.% moisture, 1.7 wt.% lipids, 62.7 wt.% dietary fiber, 2.3 wt.% ash, 17.8 wt.% carbohydrates, and 8.7 wt.% proteins. Soussi and coauthors [40] carried out the physical-chemical and composition analysis of the flour from 'Carignan' (*V. vinifera*) grape seeds and observed 12.1 wt.% moisture, 7.8 wt.% lipids, 3.4 wt.% protein, and 5.9 wt.% ashes. Prado and coauthors [34], in the characterization of seed grape after oil extraction, reported an extractives content in water of 8.1 wt.%, whereas the extractives content in ethanol was 5.3 wt.%.

Yalcin and coauthors [41] evaluated the physical-chemical composition of 'Cabernet', 'Gamay', 'Kalecik Karasi', 'Okuzgozu', and 'Senso' grapes grown in Turkey, reporting 5.5 – 5.8 wt.% moisture, 2.1 – 2.2 wt.% ash, 12.1 – 17.1 wt.% oil, and 9.3 – 10.2 wt.% protein. Bada and coauthors [42] studied the composition of 'Tempranillo', 'Garnacha', 'Mencia', 'Carrasquín', 'Albarín', and 'Verdejo' grape seeds, reporting 10.4 – 14.1 wt.% moisture, 7.6 – 13.9 wt.% oil, and 8.1 – 10.8 wt.% protein. A similar centesimal composition observed may indicate that wastes from different grape cultivars may be suitable for similar applications, easing the process and increasing the availability of feedstock. In addition, waste management procedures, such as drying can have a negative effect on some waste properties, such as the content of bioactive and antioxidant molecules, which commonly have a thermolabile characteristic.

The GSk had the smallest pH value (3.54). The organic acids present in the wastes may influence the stability and, consequently, the color of anthocyanins, since these compounds are more stable under acidic conditions. Similar results were described by Castro-López and coauthors [43] and Bender and coauthors [37], in which the pH values of flour from grape wastes ranged between 3.3 and 3.9, being classified as acidic products.

When comparing the results of the same grape variety, variations can occur due to the composition of the fruit and, consequently, of the wastes generated. The composition is directly influenced by factors linked to the cultivation, such as edaphoclimatic factors, cultural practices, and harvesting period, among others. It is also important to point out that this variation is inherent to any agricultural waste and must be considered when conceiving possible applications for the wastes [44-45].

The wastes (GSk, GSe, and DGS) had high fiber contents, suggesting that these materials could be a source of dietary fiber, with a potential to be used as a food supplement in the formulation of dietetic products rich in fibers, such as cereal bars [46].

Agricultural and agro-industrial wastes rich in lignocellulosic fibers can also be used in the production of packages. The addition of these grape wastes to the polymer matrix may enhance the physical-chemical properties and stability of starch foams due to the composition of the wastes (mainly cellulose, hemicellulose, and lignin), which allows for better interaction between the waste and the polymer [47-49].

Contents of phenolic compounds, anthocyanins, and flavonoids

The contents of phenolic compounds, anthocyanins, and flavonoids of the wastes are shown in Table 2.

Table 2. Contents of phenolic compounds, total anthocyanins, and flavonoids of the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS).

Parameter	GSk	GSe	DGS
Phenolic compounds (1)	1,530±73 [a]	2,632±52 [b]	3,372±53 [c]
Total anthocyanins (2)	89±2 [a]	23±1 [b]	20±1 [b]
Flavonoids (3)	762±17 [a]	2,233±19 [b]	3,136±30 [c]

(1) Results expressed as milligrams-equivalent of gallic acid per 100 g of sample; (2) Results expressed as milligrams-equivalent of cyanidin-3-glycoside per 100 g of sample; (3) Results expressed as milligrams-equivalent of quercetin per 100 g of sample. GSk - grape skin; GSe - grape seed; DGS - defatted seed grape with skin fragments. Means in row followed by the same superscript letter do not differ statistically by Tukey's multiple range test at 5 % error probability ($p < 0.05$).

The DGS waste had the highest contents of phenolic compounds and flavonoids, whereas the GSk waste had the highest anthocyanin content. According to García-Lomillo and González-SanJosé [16], anthocyanins are mainly present in grape skin, while flavonoids are found mainly in the seeds. Castellanos-Gallo and coauthors [7] commented that the seeds have greater amounts of phenolic compounds, with smaller contents in the pulp, and the anthocyanins accumulate mainly in the skin, as observed in the present work.

Peixoto and coauthors [10], evaluating the phenolic profile of *V. vinifera* grapes (skin, seed, and the mixture), reported that the seed had greater amounts of phenolic compounds while the skins had higher anthocyanin contents. In addition, these byproducts are potential sources of phenolic compounds with antioxidant and antimicrobial activities, with applications in food, pharmaceuticals, and cosmetics industries.

The content of phenolic compounds in the GSk waste was 1,530 $mgA_{GE}{\cdot}100\ g^{-1}$. This is like the values reported by Haas and coauthors [50], who observed phenolic content in the range of 1,381 – 1,700 $mg_{AGE}{\cdot}100\ g^{-1}$ for organic 'Ives noir' grape marc. Raota and coauthors [51] reported a phenolic content of 1,790 $mg_{AGE}{\cdot}100\ g^{-1}$ for the same kind of waste from wine processing. Karnopp and coauthors [38] reported phenolic content of 1,977 $mg_{AGE}{\cdot}100\ g^{-1}$ for the flour of organic 'Ives noir' grape skin. Lago-Vanzela and coauthors [3] reported, for 'Ives noir' grapes grown in São Paulo state (Southeast Brazil), anthocyanin content of 136 $mg{\cdot}100g^{-1}$ and phenolic compounds content of 113 $mg_{GAE}{\cdot}100\ g^{-1}$, distributed between the skin (93.7 %) and the pulp (6.3 %).

The anthocyanins content in GSk waste was 89 $mg_{CGE}{\cdot}100\ g^{-1}$. Haas and coauthors [50] reported anthocyanin content of 151.3 $mg_{CGE}{\cdot}100\ g^{-1}$, 147.0 $mg_{CGE}{\cdot}100\ g^{-1}$, and 177.7 $mg_{CGE}{\cdot}100\ g^{-1}$ for 'Ives noir' grape marc dried at 45 °C, 55 °C, and 65 °C, respectively. Karnopp and coauthors [38], characterizing the flour of organic 'Ives noir' grape skin, observed an anthocyanin content of 102.8 $mg_{CGE}{\cdot}100\ g^{-1}$.

Deng and Zhao [36] reported anthocyanin content of 142 $mg_{mal\text{-}3\text{-}glu}{\cdot}100\ g^{-1}$ in the wastes of grape skin from the winemaking of 'Merlot' grapes, 89 $mg_{mal\text{-}3\text{-}glu}{\cdot}100\ g^{-1}$ for 'Cabernet Sauvignon' variety, and 29 $mg_{mal\text{-}3\text{-}glu}{\cdot}100\ g^{-1}$ for 'Pinot Noir' grapes. The authors commented that, due to the thicker skins, the 'Merlot' and 'Cabernet Sauvignon' grapes had significant higher anthocyanin contents than the 'Pinot Noir' variety.

The waste from grape skin has potential uses because of the presence of phenolic compounds that are not completely and efficiently extracted during juice production. Although the juice industry use enzymes to increase the yield and facilitate the extraction of these compounds, especially the pigments that confer color to the product (anthocyanins), the waste has high content of these non-extracted compounds. Karnopp and coauthors [38] reported that grape skin waste from juice processing had higher phenolic content than the juice, especially trans-resveratrol, quercetin, and epicatechin.

Regarding the individual contents of phenolic compounds, the results are shown in Table 3.

Table 3. Individual contents of phenolic compounds in the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS), determined by HPLC.

Compound	Content (mg·kg^{-1})		
	GSk	GSe	DGS
Gallic acid	-	23.8±0.47 ^{b}	10.9±0.2 ^{c}
Epigallocatechin	67.9±0.4 ^{a}	-	-
Catechin	2.59±0.08 ^{a}	14.2±0.2 ^{b}	6.62±0.05 ^{c}
Chlorogenic acid	53.1±1.3 ^{a}	2,855±2 ^{b}	1,361±27 ^{c}
Epicatechin	14.9±0.2 ^{a}	405±2 ^{b}	208±4 ^{c}
Epigallocatechin gallate	10.8±0.2 ^{a}	-	-
Rutin	127±0.5 ^{a}	-	-
Vitexin	33.9±0.7 ^{a}	10.0±0.4 ^{b}	7.51±0.35 ^{c}
Ferulic acid	1,855±7 ^{a}	-	-
Naringin	9.83±0.31 ^{a}	-	-
Hesperidin	-	8.25±0.30 ^{b}	5.89±0.30 ^{c}
Resveratrol	1.37±0.02 ^{a}	-	-
Quercetin	1.59±0.02 ^{a}	-	-

'-' – Result below the limit of quantitation of the method (0.01 mg·kg^{-1}). GSk - grape skin; GSe - grape seed; DGS - defatted seed grape with skin fragments. Means in row followed by the same superscript letter do not differ statistically by Tukey's multiple range test at 5 % error probability ($p < 0.05$).

The phenolic compounds found in higher levels in the GSe and DGS wastes were chlorogenic acid and epicatechin, with negligible contents of epigallocatechin gallate, rutin, ferulic acid, naringin, resveratrol, and quercetin. For the GSk waste, ferulic acid and rutin were the phenolic compounds found in higher concentrations, and gallic acid and hesperidin were not identified.

Raota and coauthors [51], evaluating the phenolic composition of 'Ives noir' grape marc extracts, reported the presence of gallic acid, ferulic acid, and catechins. Karnopp and coauthors [52], characterizing the flour of organic 'Ives noir' seeds, observed the presence of gallic acid, catechin, quercetin, chlorogenic acid, resveratrol, and epigallocatechin.

Bender and coauthors [37], characterizing grape seed flour from 'Marselan' (*Vitis vinifera*) grapes from winemaking identified the presence of gallic acid, catechin, quercetin, chologenic acid, rutin, and resveratrol. Farhadi and coauthors [53] observed higher contents of catechin, epicatechin, gallic acid, and resveratrol on the skin of 'Ghara Shani' grapes, the presence of rutin and caffeic acid in the skin of the 'Ghara Shira' variety.

Taseri and coauthors [54] reported the grape marc of the 'Muscat Hamburg' variety, from the juice processing, had catechin, epicatechin, and resveratrol. However, it is important to observe that the profile and concentration of phenolic compounds can be affected by the ripening degree of the grapes, environmental conditions, and grape storage and processing after harvest [52].

Antioxidant capacity of the wastes

The results of antioxidant capacity of the wastes, based on the sweeping of the DPPH and ABTS+ radical, as well as the millimolar equivalents of Trolox®, are presented in Table 4.

Table 4. Antioxidant activity of the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS), determined by HPLC.

Parameter	GSk	GSe	DGS
Sweeping percentage of DPPH radical	79.2 ±0.8 ^{a}	84.8±0.5 ^{b}	83.2±0.6 ^{b}
Millimolar-equivalent of Trolox® (DPPH)	1.21±0.01 ^{a}	1.30±0.01 ^{b}	1.27±0.01 ^{c}
Sweeping percentage of ABTS radical	99.7±0.01 ^{a}	99.3±0.3 ^{a}	99.6±0.1 ^{a}
Millimolar-equivalent of Trolox® (ABTS)	1.53±0.01 ^{a}	1.52±0.01 ^{a}	1.53±0.01 ^{a}

CA - grape skin; SE - grape seed; DGS - defatted seed grape with skin fragments. Means in row followed by the same superscript letter do not differ statistically by Tukey's multiple range test at 5 % error probability ($p < 0.05$).

The results of antioxidant activity were higher by the $ABTS^{+}$ method in all samples, with no statistical differences between them because the $ABTS^{+}$ method has a stronger correlation with phenolic compounds content than the DPPH method [55]. However, as observed by Olszowy and Dawidowicz [56] both methods (DPPH, and $ABTS^{+}$) have an easy procedure and high stability. In addition, the use of different radicals, with

different sensibility degrees, allows for a better observation of the coverage and degree of antioxidant activity of the tested wastes.

By the DPPH method, the DGS and GSe wastes had higher antioxidant activity, while the GSk waste had lower activity. Burin and coauthors [55] observed that anthocyanins had the weakest correlation with antioxidant activity, which agrees with the data observed in this study, where the GSk waste had higher anthocyanin content and lower antioxidant activity among the wastes studied.

Pezzini and coauthors [57] reported a higher antioxidant activity by the DPPH method (74.2 %) in the wastes from the processing of 'Isabella' and 'Ives noir' grapes (*V. labrusca*) for juice production, with results like those observed in this study. Silva and coauthors [58] quantified, using the DPPH and $ABTS^+$ methods, of microcapsules from 'Isabella' grape marc, capacities antioxidant capacities in the range of 377.44±0.01 – 1,768.12±0.07 $\mu mol_{TEAC} \cdot 100\ g^{-1}$.

Monteiro and coauthors [59], evaluating the antioxidant capacity of 'Ives noir' grapes marc from juice industry, reported values of 33.3±0.5 $\mu mol_{TEAC} \cdot 100\ g^{-1}$ and 32.9±0.8 $\mu mol_{TEAC} \cdot 100\ g^{-1}$ for the DPPH and $ABTS^+$ radicals, respectively.

Content of macro and microelements

The results of mineral contents for the analyzed wastes are presented in Table 5. Minerals participate in important biological and metabolic activities by being distributed into macro elements in plant tissue in the range of $g \cdot kg^{-1}$ and microelements in the range of $mg \cdot kg^{-1}$.

Table 5. Macronutrient and micronutrient contents in the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS).

Parameter	GSk	GSe	DGS
Phosphorous ($g \cdot kg^{-1}$)	1.95±0.07 ^{a}	3.45±0.21 ^{b}	3.05±0.35 ^{b}
Sulfur ($g \cdot kg^{-1}$)	1.65±0.07 ^{a}	1.00±0.14 ^{b}	1.25±0.07 ^{c}
Potassium ($g \cdot kg^{-1}$)	14.45±0.92 ^{a}	4.29±0.09 ^{b}	3.09±0.14 ^{c}
Calcium ($g \cdot kg^{-1}$)	1.55±0.21 ^{a}	4.11±0.16 ^{b}	3.75±0.07 ^{c}
Magnesium ($g \cdot kg^{-1}$)	0.35±0.07 ^{a}	2.24±0.33 ^{b}	1.55±0.21 ^{c}
Manganese ($mg \cdot kg^{-1}$)	11.55±1.63 ^{a}	20.85±0.92 ^{b}	19.65±0.92 ^{b}
Copper ($mg \cdot kg^{-1}$)	27.45±1.34 ^{a}	11.45±0.07 ^{b}	10.1±0.2 ^{c}
Zinc ($mg \cdot kg^{-1}$)	3.65±0.78 ^{a}	9.61±0.11 ^{b}	8.6±0.42 ^{c}
Iron ($mg \cdot kg^{-1}$)	160.5±7.8 ^{a}	51.9±1.88 ^{b}	28.2±0.28 ^{c}
Boron ($mg \cdot kg^{-1}$)	88.0±8.5 ^{a}	17.7±0.71 ^{b}	12.3±3.82 ^{c}

GSk - grape skin; GSe - grape seed; DGS - defatted seed grape with skin fragments. Means in row followed by the same superscript letter do not differ statistically by Tukey's multiple range test at 5 % error probability ($p < 0.05$).

Potassium was the macro element found in the highest amount, especially in the GSk waste. This nutrient is present in the byproducts of grape processing because is an essential mineral in plant development and growth. This element accumulates mainly in grape skins and can also be used as a component of fertilizers [60]. The GSe and DGS wastes did not differ statistically regarding the phosphorous and manganese contents. Iron was the microelement found in higher amounts, and the GSk waste had the highest content among the wastes. In addition, the GSk waste had higher amounts of sulfur, copper, and boron.

Cid and coauthors [60], studying the grape marc from Turkish grape varieties, observed that, relative to microelements, copper and iron were the most abundant elements in grape skin waste, and iron was most abundant in grape seed waste. The same authors also reported that the amounts of minerals were generally higher in the skins compared to the seeds, except for calcium and magnesium in most samples.

The observed differences between the results of this work and other studies in the literature are linked to the mineral profile, which is indicative of the origin and variety of the grapes, being also related to soil composition and vineyard management practices [61-62].

Thus, the byproducts of grape processing are also rich in minerals, which represents an advantage for the use of these wastes in the food industry, such as a component of food formulations to enhance their nutritional value. Moreover, due to the high contents of minerals, these wastes could also be envisaged for agricultural uses. Cid and coauthors [60] commented that considering the contents of metals and minerals, grape marc and its derivatives could be easily used as components in the formulation of fertilizers.

FTIR and TG analyses

The FTIR-ATR spectra of the wastes are presented in Figure 2(A) and the TG and DTG curves of the wastes are presented in Figure 2(B).

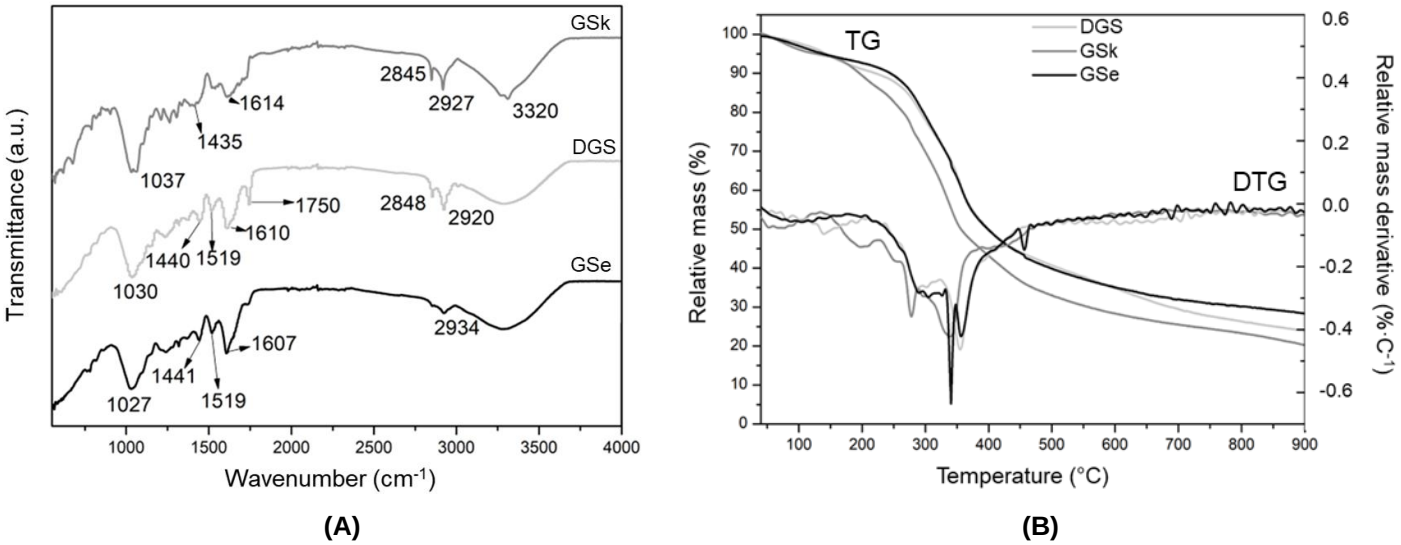

Figure 2. FTIR spectra (A) and TG/DTG curves (B) of the wastes of grape skin (GSk), grape seed (GSe), and defatted seed grape with skin fragments (DGS).

The band in the region of 3,320 cm^{-1} is related to stretching vibrations of hydroxyl groups, and the bands in the range of 2,920 – 2,930 cm^{-1} and 2,845 – 2,850 cm^{-1} are the result of asymmetric stretch vibration of CH_2 groups, mainly associated with hydrocarbon chains of lipids and lignin [13,63-64].

The band at 1,750 cm^{-1} corresponds to the absorption of carbonyl groups in ester groups, and it is related to the presence of fatty acids and glycerides, as well as pectins and lignins. The bands in the range of 1,607 – 1,614 cm^{-1} are related to the stretching of carboxyl groups and C=C aromatic moieties in phenolic compounds and pectins, for example. Bending vibrations of hydroxyl groups may also have a role. The bands of 1,519 cm^{-1} and 1,435 – 1,441 cm^{-1} are associated with C-C stretching in aromatic compounds, such as phenolic compounds. The band in the region of 1,027 – 1,037 cm^{-1} is related to C-O and O-H stretching vibrations [13,63-65]. The GSk waste had weaker absorption bands in the range of 1,440 – 1,600 cm^{-1}, which are related to phenolic compounds compared to GSe and DGS wastes. These results share the same behavior regarding the contents of phenolic compounds since the GSk waste had the lowest levels of these compounds among the three wastes.

The thermal degradation of the wastes (Figure 2B) is associated with three main decomposition stages. Hemicellulose degraded in the temperature range of 150 – 310 °C, the less stable fraction of lignin and cellulose in the range of 310 – 400 °C, and the decomposition of the most refractory fractions of lignin around 450 °C [66]. The mass losses observed up to 150 °C are related to moisture removal, volatilization of extractives, and low-mass organic molecules [66-67].

The mass losses in the temperature range of 150 – 310 °C were 27.5 %, 18.9 %, and 18.3 % for the GSk, DGS, and GSe wastes, respectively. The GSk waste had the higher mass loss at this range, probably due to the higher hemicellulose content.

In the temperature range of 310 – 400 °C, the observed mass losses were 23.6 %, 26.3 %, and 25.9 % for the GSk, DGS, and GSe wastes, respectively. The DGS and GSe wastes had greater mass losses caused by the higher lignin and cellulose contents than the GSk waste. In addition, the higher stability of GSe may be associated with the lack of grape skin fragments, which were present in DGS waste. These skin fragments can probably decompose thermally more easily due to the smaller thickness than the seed particles.

The residual waste masses at 900 °C, corresponding to ashes (mineral content) and fixed carbon, were 20.2 %, 23.9 %, and 28.3 % for the GSk, DGS, and GSe wastes, respectively. Among the wastes, GSk was the one with the lowest thermal stability. This can be seen due to the greater relative mass loss, especially at lower temperatures. Such a behavior is the result of a large fraction of this waste being composed of volatile and thermolabile compounds.

Knowing the thermal stability of the wastes matters when conceiving uses of these materials as additives in polymers. Considering that several packaging processes are carried out under high temperatures,

understanding the thermal behavior of the wastes can indicate more or less suitable ones and avoid their degradation during processing, which could have a deleterious effect on the composite material [68].

Water sorption capacity

The water sorption capacities on a dry basis of the wastes were 2.91±0.13 $g \cdot g^{-1}$, 2.22±0.05 $g \cdot g^{-1}$, and 1.84±0.03 $g \cdot g^{-1}$ for the GSk, DGS, and GSe wastes, respectively. The samples differed statistically, indicating that each material had a distinct behavior regarding this property. Sant'Anna and coauthors [69] reported water sorption capacity in the range of 3.00 – 4.25 $g \cdot g^{-1}$ for winemaking wastes.

The GSe waste had the lowest water sorption capacity compared to GSk and DGS wastes. This behavior agrees with the lipid content of the wastes. The GSk waste had the highest water sorption capacity and the lowest lignin content. According to Iriani and coauthors [70], lignin may reduce the number of available hydroxyl groups to interact with water molecules, reducing the water sorption capacity of the material.

Water sorption capacity is an important property when considering the use of these wastes in the formulation of active packaging for foods and other products. The addition of these materials may increase the shelf life of the packed material, retard package decomposition, and/or keep or enhance the condition of packed food. A high water sorption capacity is desirable for packages with hydrophilic properties, such as absorbent materials. For food that exudates liquid, absorbent materials may be used to remove this free liquid, reducing condensation, darkening, keeping the moisture, and preventing changes in food color and texture. However, it is also important to observe that the material added to the package must not cause perceptible or significant changes in the organoleptic properties of the packed food [71-72].

Potential uses for the grape wastes

In the last few decades, there are growing awareness and concern about sustainable consumption and the impact of recycling on the environment. In this sense, the reuse of wastes is a tool to reduce the environmental impact of some product chains and optimize processes. In addition, the reuse of wastes also helps the maintenance and rational use of natural resources.

Organic farming can be defined by agricultural and crop management practices without the use of synthetic or semisynthetic pesticides and fertilizers. As a result, the food obtained is free of pesticides and other undesirable substances and rich in components with nutraceutical value, such as antioxidants and vitamins, the former due to the higher content of polyphenols [73]. The use of wastes generated in grape juice and wine production and grape seed oil extraction from organic sources may be an alternative to aggregate value to the productive chain and give a proper destination in the face of current disposal methods given to these wastes.

According to García-Lomillo and González-SanJosé [16], grape marc had a high valorization potential as a byproduct in food industry. This byproduct, being from a natural source, had differentiated properties, with capacity to inhibit different microbial agents and chemical reactions, allowing for the reduction of synthetic additives, such as preservative and antioxidant agents, without compromising the quality and stability of the product.

The functional flours obtained as a product from the agricultural wastes generated in fruit and vegetable processing are already considered a sustainable option, with cost reduction and increase in profits. These flours can be used as functional ingredients in food products and other uses [74]. Studies report the potential of using the wastes generated in grape processing as additives in foods being a viable alternative to enhance the health and nutraceutical properties of the treated foods [75-76]. According to Bender and coauthors [37], grape skin flour has important amounts of fibers, carbohydrates, and inorganics (ash), as well as the presence of resveratrol, luteolin and kaempferol, antioxidant compounds with pronounced biological, pharmaceutical, and nutraceutical properties.

Pedroza and coauthors [77] evaluated the addition of dehydrated grape skins from juice industry to fresh and aged red wines to avoid degradation of color, aroma, and content of phenolic compounds before product packaging. Color degradation is a natural process that occurs in all wines due to chemical and biochemical reactions on the polyphenol with the presence of oxygen. The authors concluded that the use of dehydrated grape skins from the juice industry enhanced the color and content of phenolic compounds of the treated samples.

Toaldo and coauthors [78] noted that the addition of grape seeds to the production process of *Vitis labrusca* L. (Concord, Isabella, and Ives noir) grapes increased the amount of polyphenols and the antioxidant potential of grape juices. The authors also commented that the byproducts (skin and grape seed) had higher polyphenol content than the edible parts of the berry.

Silva and coauthors [58] reported that the use of lyophilized and microencapsulated grape extracts from Isabella grapes had a high potential to be used as a natural antioxidant in meat industry. The microencapsulated material had better performance when compared to the synthetic antioxidant commonly used (sodium erythorbate), increasing the oxidative stability of hamburgers and avoiding color changes during refrigerated storage. Cisneros-Yupanqui and coauthors [79] reported that grape marc may be a promising alternative to avoid the oxidation of corn oil.

Meini and coauthors [80] reported the potential of using grape marc as a substrate for production of industrial enzymes and gallic acid. Saadoune and coauthors [81] used the seeds from grape marc as a source of bioactive compounds in bowel diseases.

Grape marc can be a source of anthocyanins, which have antioxidant properties and prevent cardiovascular diseases [7]. Balbinoti and coauthors [82] reported that the addition of 'Ives noir' grape marc flour during rice parboiling as a source of bioactive compounds increased the contents of phenolic compounds, flavonoids, anthocyanins, and the antioxidant activity compared to the parboiled rice without grape flour.

Grape marc extracts can be used in the treatment of liquid effluents due to their antioxidant properties [83]. The applicability of these extracts is also being explored in Materials Engineering, such as in the development of natural dyes for fabric and as an additive in the formulation of active films and membranes [84-85]. Cejudo-Bastante and coauthors [86] reported the use of grape marc extract as a natural antioxidant in the development of bioactive jute fibers for food packaging, obtaining a material with a better performance regarding its food conservation potential.

CONCLUSION

The evaluated wastes had high fiber contents and are a source of minerals and bioactive compounds, such as phenolic compounds, anthocyanins, and flavonoids. This result demonstrates their potential for reuse, with value addition and a more adequate destination. The DGS waste had the highest contents of phenolic compounds and flavonoids, whereas the GSk waste had the highest anthocyanin content, which may be desirable for uses in active packaging and to improve the stability of products with these materials added. The GSe and DGS wastes had greater thermal stability, and the GSk waste had a higher water sorption capacity, giving these wastes different possible uses. In this sense, the importance of waste characterization stands out as a tool to understand the properties and possible applications of these materials because of their intrinsic variability due to origin, processing, and, in the case of agricultural wastes, crop management, and agricultural practices.

Funding: This research received no specific external funding.
Acknowledgments: The authors would like to thank the financial support received from CAPES (Coordination for the Improvement of Higher-Level Personnel, Brazil), CNPq (National Council for Scientific and Technological Development, Brazil), and FAPERGS (Research Support Foundation of the State of Rio Grande do Sul, Brazil).
Conflicts of Interest: The authors declare no conflict of interest.

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