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REVIEW ARTICLE



Strategies for recycling and valorization of grape marc

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ABSTRACT

Grapes are one of the most cultivated fruit crops worldwide. Either for wine or juice production, grape processing generates a large amount of residues that must be treated, disposed of or reused properly to reduce their pollution load before being applied to the soil. In this review, a special focus is given to the treatment and valorization of the winemaking by-product like grape marc via anaerobic digestion, composting and vermicomposting at laboratory, pilot, and industrial scales. The impact of the final products (digestates, composts, and vermicomposts) on soil properties is briefly addressed. Moreover, the role of grape marc and seeds as a valuable source of natural phytochemicals that include polyphenols and other bioactive compounds of interest for pharmaceutical, cosmetic, and food industries is also discussed. This is of paramount importance given the fact that sustainability requires the use of management and valorization strategies that allow the recovery of valuable compounds (e.g. antioxidants) with minimum disposal of waste streams.

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Introduction

Wineries constitute one of the most important agro-industrial sectors world-wide [1]. An estimation carried out by the International Organization of Vine and Wine stated that around 281 000 000 hl of wine were produced globally in the 2013/2014 campaign (<http://www.oiv.int> in [2]). This comes hand in hand with the fact that grapes are one of the most cultivated fruit crops worldwide, with the production of more than 60 million metric tons per year [3]. *Vitis vinifera* is the most commonly cultivated species for wine production, and according to the FAO [4] around 80% of its production represents 78 million tons that has been used in the wine sector.

The main concern is that the winemaking process generates, from the field to the bottle, an ample variety of solid and liquid by-products including vine shoots, grape marc or grape pomace, wine lees, spent filter cakes, vinasses, and winery wastewater that must be treated, disposed of or reused properly in order to avoid negative environmental impacts [3,5] (Figure 1). Therefore, special attention has been given to more profitable and sustainable options by both the scientific community and producers aiming at maximum utilization of all raw materials and by-products derived from

the wine industry ultimately reducing to a minimum the disposal of waste streams [6] (Figure 2).

During wine production, approximately 25% of the grape mass results in grape marc that mainly consists of the stalks, the skin, the disrupted cells from the grape pulp and the seeds that remain after the grape crushing and pressing steps carried out to obtain the stem or grape juice [3,7–9]. It is estimated that the production of 6 L of wine renders approximately 1 kg of grape marc that accounts for worldwide production of 10.5–13.1 Mtons of grape marc annually. Grape marc is characterized by large quantities of soluble sugars that can be further used for ethanol fermentation rendering a beverage known as grape spirit that arises after grapes are pressed to juice for white winemaking, and after fermentation for red winemaking [10]. Moreover, fermentation of the residual sugars can increase the economic value of grape marc by providing industrial ethanol for cosmetic and pharmaceutical uses. Additionally, grape marc has the potential to be a competitive and valuable alternative to replace fossil fuels by means of bioethanol production [6].

Furthermore, grape marc has been used as an additive in animal feeding [11], even though its high content in polymeric polyphenols may reduce its

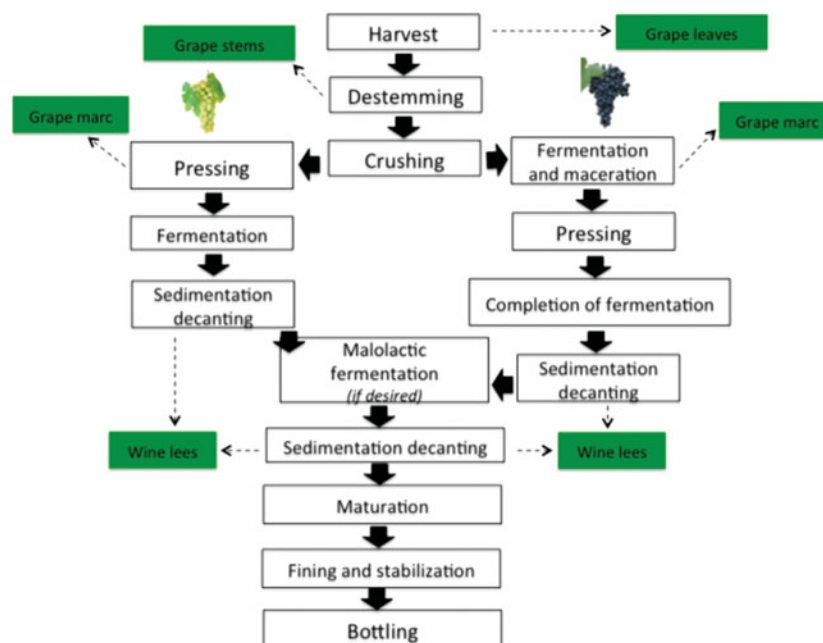


Figure 1. Overview of the steps and by-products generated during wine processing (modified from Devesa-Rey et al. [3]).

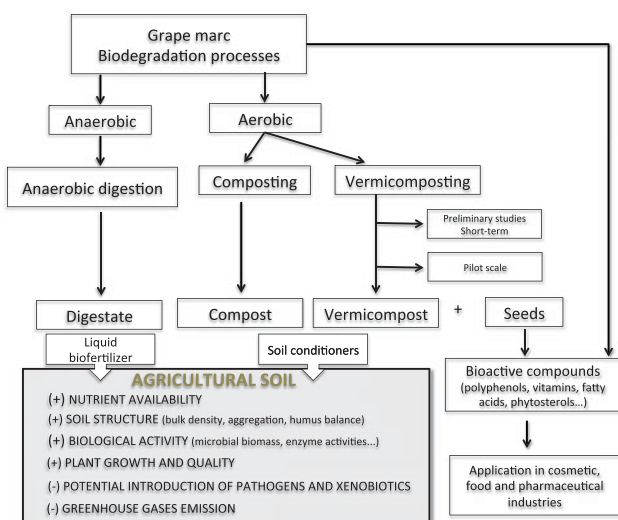


Figure 2. Schematic diagram for the valorization of the grape marc via aerobic and anaerobic biodegradation processes, along with the positive (+) and negative (−) effects of the final products (compost, vermicompost, and digestate) on soil.

digestibility since these compounds can negatively affect the activity of cellulolytic and proteolytic enzymes and the growth of rumen microorganisms. The use of grape marc as an organic soil amendment also seems to be an optimal option for its valorization, since it contains significant amounts of organic matter and macronutrients [12–14]. However, its direct application into soils may cause phytotoxic and antimicrobial effects due to the release of tannins and polyphenols, which could have a negative impact on plant growth [11]. Other potentially adverse effects include soil

oxygen depletion, groundwater pollution and greenhouse gases emissions [15].

The treatment of grape marc by using appropriate management technologies could therefore reduce these environmental risks before being applied to soil. In this regard, the biological treatment of grape marc through aerobic and anaerobic biodegradation processes could be an appropriate alternative to handle and process these wastes from winery industries offering solutions to an environmental problem and obtaining derivate economic benefits from the commercialization of the manufactured products [10]. Composting has been successfully and widely used for processing grape marc under aerobic conditions with a dual purpose, i.e. environmental protection and fertilizer production [16–32] (Figure 2). Paradelo et al. [32] found, however, drawbacks when raw grape marc was composted alone; and when acid-hydrolyzed marc, which is the residue generated after pretreatment for lignocellulosic bio-ethanol production, was composted together with vinification lees at a lab-scale. These potential difficulties relied on the too intense acidic pH levels mainly for the hydrolyzed grape marc, which negatively affected microbial activity and the transition from mesophilic to thermophilic composting stages. Co-composting of winery wastes with other organic materials (e.g. organic fraction of municipal solid wastes) might help neutralize the acidity associated with grape marc [33,34] and in turn, favor the dynamics of the composting process and ultimately the quality of the final compost. Along with traditional composting, vermicomposting of grape

Table 1. Overview of the physico-chemical properties of the raw grape marc, and the final products (compost and vermicompost) derived from aerobic processes.

| | Raw grape marc | Compost | Vermicompost |
|--|----------------|------------|--------------|
| pH | 4.4 ± 0.04 | 6.9 ± 0.04 | 7.1 ± 0.003 |
| Electrical conductivity (mS cm ⁻²) | 1.3 ± 0.15 | 1.8 ± 0.08 | 0.3 ± 0.009 |
| Organic matter (%) | 91 ± 0.30 | 93 ± 0.4 | 75 ± 0.34 |
| Total C (g kg ⁻¹ dw) | 484 ± 1.60 | 539 ± 0.2 | 376 ± 1.47 |
| Total N (g kg ⁻¹ dw) | 20 ± 0.62 | 19 ± 0.02 | 30 ± 0.13 |
| C to N ratio | 24 ± 0.72 | 28 ± 0.4 | 13 ± 0.07 |
| Total P (g kg ⁻¹ dw) | 4 ± 0.08 | n.a. | 8 ± 0.32 |
| Total K (g kg ⁻¹ dw) | 31 ± 0.56 | n.a. | 11 ± 0.65 |
| Lignin (g kg ⁻¹ dw) | 516 ± 9.56 | 581 ± 3.0 | 323 ± 2.36 |
| Cellulose (g kg ⁻¹ dw) | 225 ± 10.39 | 43 ± 0.2 | 58 ± 10.48 |
| Hemicellulose (g kg ⁻¹ dw) | 101 ± 1.39 | 43 ± 0.2 | 30 ± 0.54 |
| Total polyphenols (mg GAE g ⁻¹ dw) | 58 ± 10 | n.a. | 12.5 ± 0.7 |
| Total anthocyanins (mg GAE g ⁻¹ dw) | 1.25 ± 0.04 | n.a. | 0.17 ± 0.01 |

n.a.: not available.

Digestate from pure grape marc is not available since grape marc is usually used as a co-substrate in AD. Data are given on a dry weight (dw) basis. Mean values of raw grape marc and vermicompost data were taken from Domínguez et al. [9]. Compost data were taken from Paradelo et al. [32] and it refers to composting material with a degree of maturity of 150 days.

marc has also been investigated by several authors [8,9,14, 35–39] (Figure 2) and it may provide a means to overcome the limitations encountered by Paradelo et al. [32]. Anaerobic digestion (AD) has also become an upcoming technology for the treatment of different types of wastes [40] including those derived from the wine industry [6] (Figure 2).

The first part of this review provides an overview regarding the use of the abovementioned biodegradation processes (AD, composting, and vermicomposting) as sustainable strategies for processing grape marc at laboratory, pilot and industrial scales (Figure 2). Second, this review addresses the impact of the resulting final products (digestates, composts, vermicomposts, and fertilizers) on soil properties (Table 1; Figure 2). Besides its role as a soil amendment grape marc and seeds can also be considered to be a valuable source of natural phytochemicals including polyphenols and other bioactive compounds of interest that can be used as functional compounds within the pharmaceutical, cosmetic, and food sectors thanks to their antioxidant, antifungal and scavenging activities [5,11,41–46]. Therefore, the last part of this review focuses on the importance and recovery of these bioactive compounds, mainly rich-polyphenols extracts, from the grape marc and the seeds so as to further exploit their nutritional and health-promoting effects (Figure 2).

Anaerobic digestion as an option for grape marc treatment

Anaerobic digestion has become an important technology for recycling wastes from different origins owing to the decrease in fossil fuel reserves and the production of biogas which can be used as an eco-friendly energy source [40]. The AD process involves the degradation of

organic substrates into biogas (~70% CH₄ and 30% CO₂) through the action of a microbial consortium composed of hydrolytic, acidogenic, and acetogenic bacteria, as well as methanogenic archaea that act successively during AD [40]. The sustainability of biogas production depends, however, on the proper use of the digested material [40]. In this sense, the use of digestates as organic fertilizers seems to be an optimal option for their valorization since they are known to increase soil microbial biomass and metabolic activities [47–49]. In addition, they contain significant amounts of residual organic C and nutrients (N, P, and K) for plants [50]. The magnitude of nutrient accumulation and its distribution in the soil profile following digestate application may vary depending on the soil type, the climate, the application frequency and the properties of the digestate itself [40].

Among winery by-products, wine lees and vinasses have been treated by AD [51] considering their high levels of chemical oxygen demand, both particulate and soluble, and high biodegradability [52]. These latter authors observed, at a pilot scale, that the mesophilic anaerobic codigestion of waste activated sludge and wine less resulted in enhancement of the biogas yield and process stability which may be attributed to a *priming effect* [51]. Insam and Markt [53] have recently adopted the term “*priming effect*” also for AD. This triggering effect refers to an increase of internal microbial metabolism through addition of fresh organic material that brings in energy in form of nutrients (e.g. glucose, amino acids, etc.). This results in an increase of respiratory activity and activates dormant microorganisms [54]. In addition, nutrient imbalances may be compensated by allowing enhanced microbial growth rates [54].

Da Ros et al. [55] also found that the potential methane production from different winery solid wastes

(i.e. fermented and fresh grape marc, grape stalks and wine lees) significantly increased under thermophilic conditions (55 °C), in both batch and continuous processes. Fabbri et al. [56] reported that the use of white grape marc resulting from *Nero Buono* and *Greco* grape varieties processing for AD rendered a higher biogas yield (0.273 m³ CH₄/kg volatile solids) compared to red grape marc (0.101 m³ CH₄/kg volatile solids), which highlights that the type of grape is an important factor affecting biogas production [55]. Simulation studies have also shown that it is possible to obtain 94 kWh per ton of grape marc, covering up to 45% of the energy requirements for the winemaking process [57]. However, when the anaerobic reactor is fed with only grape stalks, the production of biogas is generally lower (0.098–0.180 m³ CH₄/kg VS) due to the presence of considerable levels of recalcitrant compounds including lignin and polyphenols that are difficult to degrade under anaerobic conditions [52]. Contrarily, the incorporation of grape seeds into a laboratory scale reactor fed with fresh grape marc showed enhanced biogas production [58]. In addition, the use of grinding as a mechanical pretreatment resulted in higher methane potential when grape marc, pulp and seeds were used as feedstocks during a batch AD test [59]. These authors found a substantial increase in the anaerobic biodegradability of all of these substrates, particularly for the seeds. This could be due to the fact that the oil released from the grape seeds favored the production of methane and biogas [60]; and/or the grinding of the seeds increased their surface area contributing to lignin degradation [57]. This opens new avenues for the optimal management of grape marc as a standalone feedstock or in combination with other feedstocks such as wine lees by AD and its valorization for energy production [61]. In line with this, Lempereur and Penavayre [62] evaluated grape marc digestion from a technical, economic and environmental viewpoint in comparison with alternatives such as distillation, spreading and composting. For AD, transport and processing costs were estimated to be between €5–25/ton and €20–82.5/ton, respectively, even though these calculations may vary depending on the winery production size and whether the winery was responsible for the majority of transport and processing costs [62]. In the case of composting, these authors estimated between €63 and 100/ton for transport and processing costs [62]. In general, they found AD to be favorable from an environmental perspective when compared to alternatives after performing a life-cycle analysis against human health, ecosystem fitness, climate change, and resources impact indicators [10,62].

Nonetheless, there is still scarce information about how the achievements obtained from lab-scale AD studies can be extrapolated to a full-scale digester [59]. Moreover, the impact of digestates obtained after AD of grape marc on soil biota and nutrient cycling is in its infancy and there is the need of digging deeper into these aspects in order to promote AD as a sustainable strategy for processing grape marc and other winery wastes.

Aerobic processes as options for grape marc treatment: composting and vermicomposting

Composting and vermicomposting are considered two of the best-known and environmentally sound approaches for the recycling and valorization of a wide variety of solid organic wastes under aerobic conditions [63–66], by transforming them into a nutrient-rich, microbiologically active and stabilized peat-like material known as composts and vermicomposts. These final products have been found to provide numerous benefits when used as soil amendments in greenhouse and field studies [6,66], as they increase soil organic matter levels, soil porosity, and aggregate stability. They may also foster nutrient availability leading to an increase in soil microbial biomass and activity [67], which could be attributed to the activation of the indigenous soil microbiota due to the supply of C-rich organic compounds present in the (vermi)composts [63,65]. A shift in soil pH after the application of (vermi)compost amendments may also lead to important changes in the composition and diversity of soil microbial communities [68], since pH is often correlated with underlying environmental factors influencing the microbial community such as nutrient availability [69]; the synthesis and activity of soil enzymes [68]; and the heavy metal availability and toxicity [70] owing to the strong effects of pH on the solubility and speciation of metals both in the soil as a whole and particularly in the soil solution. A comprehensive meta-analysis of 690 independent experiments compared the performance of organic amendments and mineral-only fertilization on crop yields, and they concluded that crops responded better to organic amendments when soil pH ranged from weak-acidic to weak-alkaline levels [68].

The value of compost from grape marc has already been discussed by Graefe [71] and Streichsbier et al. [72] who suggested both the production of energy and humified products for soil amelioration. Some recent findings have contributed to broaden our knowledge about whether and to what extent (vermi)compost amendments derived from winery by-products and, in

particular from grape marc have significant impact on soil properties and plant growth. In this context, Paradelo et al. [31] observed that the use of grape marc composts as peat substitutes did not show any prejudicial effect on the final biomass production and the number of plants grown (*Hordeum vulgare* L.) with respect to the control substrates, even though there was a delay in plant germination after seeding. Moldes et al. [25] reported that biodegraded grape marc derived from a 60-day composting period resulted in a germination index of 155% with regard to the growth of ray grass seeds. In an experiment comparing different organic fertilizers, Insam and Merschak [73] observed that plant cover (grasses, herbs, and mosses) was promoted by Biovin[®], a product derived from grape marc compost. Moreover, the nitrogen losses were lowest in the Biovin[®] amended soil cores, suggesting a retarded microbial turnover of the added organic matter making the product act like a slow-release fertilizer. Requejo et al. [13] also found that the addition of grape marc-derived compost had a positive effect on P availability in calcareous soils despite the fact that the presence of phenolic compounds in this winery by-product may prevent P adsorption in these soils. Moreover, due to the lignocellulosic nature of grape marc, the resulting vermicomposts were characterized by a good sorption potential for nonionic pesticides such as imidacloprid and diuron as pointed out by Romero et al. [74] and Fernández-Bayo et al. [22,75,76]. In fact, Fernández-Bayo et al. [22] found that the addition of this type of vermicomposts significantly reduced the leaching of diuron, imidacloprid and their metabolites throughout experimental soil columns probably due to increased adsorption of these pesticides to the organic matter of winery vermicomposts. Furthermore, Romero et al. [74] observed that the reduction in diuron concentrations in soils treated with grape marc-derived vermicompost was accompanied by an increase in dehydrogenase activity underlining the degradation capacity of soil microbial communities with regard to this ureic herbicide. Indeed, the activities of several enzymes are known to increase, at rates equivalent to mineral fertilizers, after the application of vermicomposts [66]. Lazcano and Domínguez [66] reported higher β -glucosidase, alkaline phosphomonoesterase and protease activities in manure- and vermicompost-amended soils than in those treated with inorganic fertilizer, despite the low dose used (25% of total fertilization) and the short duration of the experiment (four months). Such an increase in the abovementioned extracellular enzyme activities was accompanied by higher bacterial growth rates after the application of

both organic substrates into the soil. However, no changes were recorded for fungal growth indicating that other factors, different from the fertilizer type employed, limited fungal growth. Overall, soil pH together with soil organic carbon and microbial biomass pools were found to be the main factors regulating the synthesis and activity of soil enzymes [68]. It has also been shown that the activity of these extracellular enzymes remains high in the mature vermicompost as a result of the higher degree of stabilization of enzymes to humic substances whose concentration increases as vermicomposting progresses [77]. In addition, Sánchez-Hernández and Domínguez [78] reported high levels of detoxifying enzymes (laccases and peroxidases) in grape marc- and spent coffee ground-derived vermicomposts, which underscores the potential use of these types of vermicomposts during the bioremediation of polluted soils [78]. There is, however, a knowledge gap about the distribution, stability and reactivity of vermicompost-specific enzymes in soil despite their important role in soil restoration and bioremediation [78].

Several studies have also demonstrated the potential of vermicomposts as bioactive organic materials through the isolation of various bacterial taxa that are useful for different biotechnological purposes [79–81]. In fact, Fernández-Gómez et al. [79] detected the presence of *Streptomyces* spp. in vermicompost produced from spent grape marc and lees cake, which underpins the role of vermicomposts in the biocontrol of soil-borne plant diseases caused by pathogenic fungi. As reviewed by Gómez-Brandón and Domínguez [65], there is indeed a large body of scientific evidence dealing with the positive effects of vermicomposts on the suppression of plant diseases, as well as on the incidence and abundance of plant-parasitic nematodes and arthropod pests in soil. For instance, Szczech [82] found that addition of solid vermicompost to tomato seeds greatly reduced the infection caused by the pathogenic fungi *Fusarium lycopersici*. The application of vermicompost extracts as foliar sprays in pea and tomato plants diminished the incidence of fungal diseases such as *Phytophthora infestans* [83]. Edwards et al. [84] observed that the suppressive effect of vermicompost on several plant pathogens (i.e. *Pythium*, *Rhizoctonia*, *Verticillium*, and *Plectosporium*) disappeared after sterilization of the vermicompost. These effects point out the presence of biological suppressive agents in vermicompost capable of disease reduction. Nonetheless, further research about the potential mechanisms responsible for these suppressive effects and the main factors involved is required.

Overall, the aforementioned reinforces that the biological component (i.e. the microbial community composition, and microbial activity) of a vermicompost may play a key role in its usefulness in agriculture [66] and other applications like the remediation and restoration of contaminated soils [75,76].

The vermicomposting process

Unlike composting, vermicomposting depends on joint action between detritivorous earthworms and microorganisms and does not involve a thermophilic phase as classical composting does. Two different phases in relation to earthworm activity are involved in the vermicomposting process: (a) an *active phase* during which earthworms ingest, process, and digest the organic matter, thereby modifying its physical-chemical and microbial composition [65,85] and (b) a *maturation phase*, during which the earthworms move toward fresher layers of the substrate, while microorganisms take over the decomposition of the earthworm-processed substrate [65].

The first step in earthworm-microorganism interactions comprises the ingestion, digestion, and assimilation of organic material in the earthworm gut and then casting [86]. Previous studies have investigated the role of the earthworm gut and its associated microbiota as a selective filter for those microbial communities present in the ingested material [36,65,85–87]. This may lead to a more active and specialized microbial community in the egested materials via increasing the rates of cellulytic metabolism and/or microbial metabolic capabilities during the passage of organic material through the earthworm gut [87]. All these changes are expected to ultimately influence the dynamics of the vermicomposting process, likely enhancing the rates of organic matter decomposition and nutrient turnover during the process [86]. As the modified microbial communities that pass through the gut transit are released into the environment as part of earthworm casts. It is expected that the inputs of those communities to fresh organic matter promote modifications similar to those observed when earthworms are present [65].

Along these lines, Gómez-Brandón et al. [36] found, on a laboratory scale, that earthworms' activity (*Eisenia andrei*) promoted the stabilization of grape marc after only two weeks of vermicomposting, as reflected by a reduction in the labile C pool and microbial biomass and activity relative to control treatment in the absence of earthworms. This reinforces the significant role of earthworms in the stabilization of the ingested substrate in the short-term, via their effects on organic

matter decomposition and microbial communities through gut associated processes. Nogales et al. [38] also observed that the combined action of earthworms and microorganisms enhanced biodegradation of different winery wastes (grape marc, vinasse biosolids, lees cakes, and vine shoots) over the course of a 16-week laboratory trial. This was supported by the depletion of hydrolytic enzyme activities such as β -glucosidase, especially during the final stages of the vermicomposting process, probably due to the depletion of readily available organic substrates throughout the process. Urease activity also followed a decreasing trend over the course of the vermicomposting process. Nonetheless, phosphatase activity was stabilized towards the end of the process suggesting that the studied feedstock contained sufficient available organic phosphorus to maintain this activity or to immobilize this enzyme in the microbial cells of the humus matrix. Altogether this underlines the potential of vermicomposting as a sustainable strategy for the disposal of grape marc and other winery wastes. However, it is necessary to evaluate the feasibility of grape marc in large-scale systems, that is, vermicomposting systems designed to deal with large amounts of wastes [8,9].

In particular, Domínguez et al. [8] demonstrated the potential of using a continuous-feeding vermicomposting system for processing grape marc on a pilot scale, registering a reduction of the initial mass of grape marc by approximately 60% as a result of the earthworm activity. On the one hand, this mass loss resulted in a higher concentration and availability of mineral nutrients in the final vermicompost. On the other hand, it also led to an increase in grape seed density. As pointed out by Domínguez et al. [8,9], the seeds can easily be separated from the vermicompost through sieving which constitutes an important step in order to obtain a stable and mature polyphenol-free vermicompost with great potential as a soil amendment [88]. Additionally, the recovery of seeds after vermicomposting has another purpose, it is to benefit from their high polyphenol (circa 60%; [89]) content along with other bioactive compounds of interest for their further use in the food, pharmaceutical and cosmetic industries. Bearing this in mind, the sieving procedure is preferably conducted during the early stages of the process, between the 4th and the 6th week of vermicomposting [9], due to the fact that the polyphenol content of the vermicomposted grape marc and seeds gradually decreases throughout the process [8]. In fact, Domínguez et al. [8] observed that after two weeks of vermicomposting the grape seeds still contained useful concentrations of phenolic acids and certain flavonols,

which make them a relevant source for exploiting their beneficial properties on an industrial scale.

Taken together, this highlights the potential of vermicomposting as an effective, simple, and environmental-friendly process that can be scaled up for industrial application producing an ample variety of added-value products from the initial grape marc.

Bioactive products: adding value to the grape marc

Over recent years, researchers, producers, and consumers have increased their awareness and demand for natural and safer additives in the food industry. In this regard, polyphenols are considered to be one of the most widely occurring groups of natural phytochemicals with therapeutic and health-promoting effects [90,91], and also useful to be as functional ingredients for the food, pharmaceutical, and cosmetic industries [11,92–94]. Polyphenols are secondary plant metabolites and due to their antioxidant and scavenging activities they play an important role in the inhibition or delay of lipid peroxidation in different biological and food systems [95]. This makes polyphenols of great interest for nutraceutical purposes. They help combating some major health problems such as obesity, cardiovascular diseases, cancer, osteoporosis, arthritis, diabetes, and cholesterol [93,96]. Moreover, they can also be used as natural colorants and food preservatives [97,98], as well as being active ingredients for cosmetic products owing to their anti-ageing effects [46,99]. As a consequence, the recovery of bioactive phenolic compounds from the winemaking process has gained increasing attention worldwide. This takes into account the potential of grape marc and seeds to be valuable sources of phytochemical compounds [11,41–46,92,100–103]. This also goes hand in hand with the necessity to reduce the environmental impact of these winery by-products through their use in a sustainable manner. In particular, special attention has been paid to the grape seed's polyphenolic content. Also, their antioxidant capacity is between 5 and 9 times higher than in the whole grape marc when evaluating the same Galician white grape varieties (Albariño, Caiño, Godello, Loureiro, Torrontés, and Treixadura) [44]. Pastrana-Bonilla et al. [104] also found the highest concentration of phenolic compounds in the seeds when evaluating 10 cultivars of muscadine grapes (five bronze skin and five purple skin) grown in southern Georgia. The average total phenolic content was: 2178.8, 374.6, 23.8, and 351.6 mg/g gallic acid equivalent in seed, skin, pulp, and leaves, respectively. Similarly, Negro et al. [105] reported that the

quantity of total phenolic substances and total flavonoids contained in the grape seed extract (8.58 g/100 g dry matter) was higher than that obtained from the peel (3.33 g/100 g dry matter) and the marc (4.19 g/100 g dry matter).

As reviewed by Fontana et al. [11], the phenolic compounds present in grapes and wine can mainly be classified into: (a) *phenolic acids* (primarily benzoic and hydroxycinnamic acids); (b) *simple flavonoids* including catechins, flavonols, and anthocyanins; and (c) *tannins* and *proanthocyanidins*. Protocatechuic acid was found as one of the most dominant hydroxybenzoic acids in grape marc from some red varieties [102], and in grape seeds from both red and white grapes [106]. Quercetin-3-O-glucuronide was determined as the main flavonol in dry grape marc [107]. Also, the amount of condensed tannins can be up to 52% in grape marc on a dry weight basis [108].

The importance of polyphenols for the winemaking process relies on their sensorial properties, as they are responsible for the primary characteristics (i.e. color and sensorial attributes such as astringency or bitterness) of the wine [109]. Several factors including the conduction and the irrigation systems, the vintage, the maturity of the fruit, the climate and/or the grape variety largely influence the concentration of polyphenolic compounds in the grape marc [42,92]. However, one of the main features that will influence the polyphenolic content of grape marc is the type of winemaking. In particular, grape marc from red wines vinification will retain less proportion of the initial grape polyphenolic content than white grape marc, due to the fact that the skins and seeds usually remain in contact with the fermentation broth for several days in red winemaking. On the contrary, since in the winemaking process white wines are elaborated with a minimal contact of the skin, or even without any, the grape marc retains much of the grape's initial polyphenols. In fact, according to González-Centeno et al. [110], and based on four white different cultivars of *Vitis vinifera* (Chardonnay, Macabeu, Parellada, Premsal Blanc), there exist no major differences between red and white varieties concerning their polyphenol profile except for the lack of anthocyanins in the white grape marc.

Due to sample complexity, it is of utmost importance to choose a suitable extraction method in order to obtain high recoveries of bioactive polyphenols from the grape marc. Conventional extraction techniques (e.g. solid–liquid extraction, heating, or grinding) have been gradually replaced by novel extraction methods that involve reduced extraction times and sample preparation, as well as low consumption of organic solvents

so as to increase extraction yields preserving high extract quality and reducing the energy consumption (the so-called green extraction concept [111]). The advantages and drawbacks of the most widely used conventional and novel extraction techniques used for the recovery of polyphenols from the grape marc and other winery by-products have recently been reviewed [11,43,112].

To date, the extraction of polyphenols has been focused on red winemaking products. Nonetheless, there are recent studies from Álvarez-Casas et al. [41,42] in which they optimized and applied for the first time at a lab-scale pressurized liquid extraction (PLE) for the recovery of polyphenols from marc derived from six white varieties (Albariño, Caiño blanco, Godello, Loureiro, Torrontes, and Treixadura) cultivated in protected areas of production in Galicia (NW Spain). Additionally, the marc obtained in the winemaking of non-native varieties grown experimentally in the region (Chardonnay, Gewürztraminer, Pinot blanc, Pinot gris, Riesling, and Sauvignon blanc) have been included in this study and compared with the native varieties [42].

Besides their polyphenolic content, grape marc and seeds can also be processed to obtain other value-added products including extracts enriched in vitamin E [113,114], which constitutes a family of lipid-soluble antioxidant compounds, containing a saturated (tocopherols) or unsaturated (tocotrienols) isoprenoid side chain linked to a phenolic-chromanol ring [11]. The importance of tocopherols relies on their activity to inhibit the peroxidation of polyunsaturated fatty acids in biological membranes [115]. They are also known to reduce the risk of cancer, cardiovascular diseases, cataracts as well as ischemia and reperfusion cell damage as reviewed by Barba et al. [43].

As pointed out by Maroun et al. [112] and Muhlack et al. [10], grape marc can also act as an important source of polysaccharides allowing the recovery of insoluble fibers such as hemicelluloses that help to regulate the intestinal tract acting as food supplements; or pectins which can be used for industrial purposes (i.e. manufacture of jams and jellies) due to their thickening and gelling properties. Apolinar-Valiente et al. [116] observed that the grape origin greatly affected the amount of cell wall material isolated from the skins of Monastrell grapes grown in three different terroirs (Cañada Judío, Albatana, and Bullas) in the province of Murcia (SE Spain); as well as the carbohydrate composition of the cell wall and in lignin and proteins. Additionally, these authors found that the enological treatment (i.e. addition of enzymatic preparation and β -galactosidase separately and dry ice addition) may

also affect the composition of marc skin cell wall material [116].

Furthermore, grape marc can be exploited toward the recovery of grape seed oil [117], which is characterized by a constant fatty acid profile, where linoleic acid (18:2 ω 6) appears to be the most abundant fatty acid, as it can contribute between 60 and 75% of the total fatty acids present in the oil [118,119]. It is an essential omega-6 fatty acid and has an important role for the development and maintenance of the nervous system and other physiological functions in humans. Oleic acid (18:1 ω 9) also occurs in a lower amounts (10–20%; [118]), together with saturated fatty acids such as stearic acid (18:0; 2–4%) and palmitic acid (C16:0; around 7%). Moreover, grape seed oil is also enriched in phytoosterols and vitamin E active compounds (tocopherols/tocotrienols) that confer it a high antioxidant activity [6]. Altogether, it makes the grape-seed oil a high-quality nutritional oil with high commercial value, and increasingly attractive in medical, cosmetic, and pharmaceutical applications [119]. Mateo and Maicas [2] have also reported that the use of microbiological processes instead of physical and chemical procedures can constitute a new frontier in by-products valorization within the wine industry allowing the production of added-value products such as edible mushrooms, biofuels, organic acids, polymers, and enzymes.

A comparison of technology options for grape marc valorization

The major goal of green technologies for the extraction of bioactive compounds from natural sources like winery wastes and by-products is to achieve a faster extraction rate and more effective energy use, increase mass, and heat transfer, reduce both the equipment size and the number of processing steps and preserve the natural environment and its resources [120].

Among these non-conventional technologies, it has been shown that the use of PLE resulted in higher yields of anthocyanins and other phenolics, and provided extracts with higher antioxidant capacities when compared to supercritical fluid extraction (SFE) after analyzing marc from different varieties of red grapes (i.e. Cabernet Sauvignon, Merlot, Petit Verdot, Syrah, Tempranillo, and Tintilla [121]). The PLE technique is based on the use of high temperatures and pressures in order to increase the efficiency of the extraction process. Increased temperature accelerates the extraction kinetics, and elevated pressure maintains the solvent below its boiling point. This results in an increase in the solubility of the analyte and its desorption kinetic rate from the sample matrix.

This accelerates, in this way, the extraction procedure and reduces not only overall solvent consumption but also the sample preparation time. The stability of phenolic compounds using superheated solvents has previously been demonstrated by Palma et al. [122] with grapes. In line with this observation, Solyom et al. [123] examined the thermal degradation of grape marc at three temperatures (80, 100, and 150 °C) and they observed that the grape marc was more sensitive by one order of magnitude to heat than its filtered extract by using simulated degradation under isothermal heating. This tendency was also confirmed by analyses of the total phenolic content and the antioxidant activity [123].

Microwave assisted extraction (MAE) has also been used to recover high-added value compounds such as polyphenols from grape skins [124], grape juice [125], and grape peel [126] in the laboratory. The MAE process involves quick heating, a reduced thermal gradient and a reduced equipment size rendering higher yields of these bioactive compounds in a very short time period. In fact, Liazid et al. [124] reported notable reductions in the extraction time from 5 h to 5 min by using MAE instead of conventional solid–liquid extraction techniques for the recovery of anthocyanins from grape skins with the variety Tintilla de Rota. Although MAE has been proposed for possible industrialization with regard to the recovery of essential oil from aromatic herbs [127] and the separation of volatile and nonvolatile organic compounds of boldo leaves [128], the feasibility of using the MAE process for extraction of bioactive compounds from winery wastes at an industrial scale is still in its infancy [43].

The matrix solid-phase dispersion (MSPD) process has also been successfully applied to the recovery of polyphenolic compounds from red and white winemaking by-products [45,129]. This latter approach has been found more advantageous when compared to the classical extraction procedures, since the entire sample is exposed to the extractant resulting in a simpler, faster (15 min on average), and more economic (about 0.5 €/per extract) alternative [129]. Moreover, it offers the possibility of assessing the extraction and clean-up at the same time reducing the chance of sample contamination [130].

The no-need of instrumentation in the application of MSPD at the laboratory scale made it *a priori* a good candidate for scaling-up the extraction process, looking for a simple, inexpensive and efficient method that allows obtaining polyphenol-enriched extracts on the industrial scale. On this basis, the research group LIDSA from the University of Santiago de Compostela has recently developed an extraction method based on the fundamentals of this technique, that can be easily scaled up for

industrial application, allowing to obtain polyphenolic extracts from a wide variety of white grape by-products such as grape marc, lees, pulp, skin, and seeds [131,132].

It has been reviewed by Barba et al. [43] that other alternatives to these solvent-based extraction methods can be the use of high voltage electric field methods, such as pulsed electric field (PEF) and high voltage electric discharge (HVED), in order to improve the extraction processes of valuable compounds from winery wastes and by-products by increasing the permeabilization of cell membranes as a result of the electroporation phenomenon. The application of electric fields within a range of temperatures between 20 °C and 50 °C damages cells from the grape skin and allows an easier extraction of soluble intracellular components through enhanced diffusion in an aqueous liquid [10]. Indeed, greater polyphenol yield were obtained in HVED extracts from grape seeds and vine shots in comparison to grinding and ultrasound treatments [133]. Several workers have also reported the efficiency of using PEF for the enhancement of polyphenol extraction from grape by-products [134,135]. Recently, Brianceau et al. [135] demonstrated that grape densification (compaction) in combination with PEF treatment rendered higher yields of polyphenols in fermented red grape marc extracts owing to better electrical conductivity in those treatments with a higher compaction. These authors underpinned the selective nature of PEF techniques with regard to the extraction of certain anthocyanins, which offers an opportunity to produce extracts with different biochemical compositions. Moreover, this technique involves less output current and with lower specific energy, along with a reduced solvent amount and extraction time than conventional treatments (i.e. grinding and dehydration) [135]. All in all, this makes PEF advantageous for industrial implementation and exploitation, even though there are still some technological challenges that should be overcome prior to this like the optimization of the treatment chamber design, since PEF treatment should be preferably performed in a continuous flow system [135]. Along with PEF and HVED, the application of pulse ohmic heating (POH), which involves an increase in the temperature by ionic movements following the application of PEF treatment, which could also be a useful tool to recover polyphenols from grape marc [136].

Conclusions

Grape processing for wine production generates large amounts of residues that must be properly disposed of. The scientific community and producers have recently

focused their interest towards more profitable and so-called sustainable options that allows, on the one hand, management and valorization of the winemaking by-products; and, on the other hand, the recovery and recycling of other bioactive compounds of interest (e.g. antioxidants) by using “greener”, non-conventional and scalable technologies. The efficiency of these technologies for the recovery of high-added value compounds from winery wastes and by-products has been investigated and is being investigated at laboratory and pilot scales. All in all, this has allowed researchers and wine producers to establish the basis for a joint effort in scaling up these technologies to be possibly industrialized. To date, some of the technologies summarized in this review have already being implemented at an industrial scale, while others are still in the first stages of development for potential industrialization.

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