## **Agri-Food Waste**

Subjects: Agriculture, Dairy & Animal Science Contributor: Valentina Melini

Agri-Food Waste (AFW) originates throughout the whole food supply chain, from production to post-harvesting, industrial processing, distribution, domestic processing, and consumption, with wastage volumes differing among phases and food commodities.

Conventional management of food waste encompasses production of renewable energy, animal feeds, and compost. Alternative pathways include the valorization of food waste as a source of bioactive compounds, such as phenolic compounds, to be used as functional food ingredients or nutraceuticals.

Drying and size reduction techniques, extraction methods, and fermentation are the main strategies to turn AFW into functional ingredients.

Keywords: food waste ; phenolic compounds ; antioxidant capacity ; bread ; functional foods ; bioavailability ; bioactive compounds

### 1. Introduction

FAO estimated that 1.3 billion tons of food, about one-third of the annual production for human use, is globally lost or wasted every year<sup>[1]</sup>. Food loss and waste equal a major loss of earth resources, such as land, water, and energy, and lead to greater greenhouse gas emissions, so as to contribute to climate change.

Agri-Food Waste (AFW) originates throughout the whole food supply chain, from production to post-harvesting, industrial processing, distribution, domestic processing, and consumption, with wastage volumes differing among phases and food commodities. In Europe, households contribute the most to food waste, with a share of 53%, followed by processing, which accounts for 19% of total food waste. The remaining 28% comes from food service (12%), production (11%), and wholesale and retail  $(5\%)^{[2]}$ .

So far, campaigns have been put in place to reduce food waste at the household level, while several strategies have been identified to reduce food waste from industrial processing and manufacturing. Conventional management of food waste encompasses production of renewable energy, animal feeds, and compost. Alternative pathways include the valorization of food waste as a source of bioactive compounds to be used as functional food ingredients or nutraceuticals<sup>[3]</sup>.

# 2. Functional Ingredients from Agri-Food Waste: Recovery of Phenolic Compounds

Food industrial processing generates specific commodity by-products. Fruit and vegetables produce great amounts of peelings, pomace, trimmings, seeds, stones, stems, and leaves<sup>[4]</sup>. Cereal grain milling generates bran, which accounts for 3-30% of the kernel weight on a dry basis, hulls, husks (4–14%), germ, broken grains (6–13%), and powders (7–12%)<sup>[5]</sup>. The legume industry produces great amounts of husks, pods, and off-quality grains<sup>[4]</sup>. Hulls, husks, skins, shells, and shattered cotyledons are the main waste of primary processing of nuts and oilseeds<sup>[5]</sup>.

Within the current bioeconomy and sustainability framework, alternative handling of these by-products encompasses the recovery of bioactive molecules, including phenolic compounds (PCs).

Drying and size reduction techniques, extraction methods, and fermentation are the main strategies to turn AFW into functional ingredients.

#### 2.1. Drying and Size Reduction Techniques

Food powders and flours are the simplest form into which AFW can be processed to be incorporated as a functional ingredient into conventional foods. The unit operations to get food powders and flours from AFW generally depend on the form of waste, which can be either liquid, solid, or a paste. In case of liquid waste, powders and flours are produced by applying a drying technique, while in case of a solid material, size reduction by crushing and grinding, milling, pulverization, granulation, and mixing must be applied<sup>[6]</sup>. Other factors affecting the choice of AFW handling methods are the heterogeneity and the structural differences of the waste, the coexistence of edible/non-edible parts<sup>[Z]</sup>, the shelf-life, and the necessity to preserve compounds of nutritional interest or with antioxidant properties.

Waste from fruit, vegetable, and oilseed processing, such as pomace, commonly undergoes first drying, then size reduction. Conventional hot-air convection drying, low-temperature vacuum drying, freeze-drying, or microwave drying are among the conventional techniques applied to reduce water content in AFW. However, the choice of the drying method must be cautious, because application of high temperatures and/or presence of oxygen may degrade thermolabile compounds or molecules sensitive to oxidation. For instance, PCs may be degraded during air-drying due to polyphenol oxydase activity<sup>[8]</sup>.

The effect of freeze-drying (FD), convective drying (CD; 50–90 °C), microwave vacuum (MWV; 120, 240, 360 and 480 W), and combination thereof on total polyphenol content in blackcurrant pomace was investigated<sup>[9]</sup>. FD determined a decrease in total polyphenols; upon CD, a linear decrease in total polyphenol content occurred at increasing temperature, except for drying at 50 °C, possibly due to inactivation of polyphenol oxidase. When MWV drying was applied, a lower degradation of polyphenolic compounds was observed thanks to a shorter processing time.

Hot air (HA) and microwave-assisted hot air (MWHA) drying were applied in combination with extrusion to bilberry (*Vaccinium myrtillus* L.) press cake<sup>[10]</sup>. It was observed that MWHA drying allowed a moisture content of 17 g 100 g-1 to be obtained in a shorter time (215 min) than HA (about 360 min); however, the phenolic compound content was not significantly different.

FD and oven-drying were applied to skins from two grape varieties and the effect on phenolic compound, anthocyanin, and flavonol content was investigated. FD enabled a higher preservation of bioactive molecules<sup>[11]</sup>.

Different combinations of drying temperatures and times were tested on blueberry and grape pomace in order to preserve procyanidins and anthocyanins<sup>[12]</sup>. It was found that a temperature of 40 °C in a forced-convection oven did not affect the bioactive molecule content, drying at 60 °C caused a reduction in anthocyanins, while at 125 °C a significant loss (about 52%) was observed.

Some additional drying techniques (e.g., hot air convective drying, microwave vacuum drying, intermittent microwave convective drying, industrial rotary drying, radiofrequency, osmotic agents, etc.) have been so far applied in food processing<sup>[13][14][15][16][17][18][19]</sup>, but their applicability in AFW drying and their effect on phenolic compound retention has not been yet explored.

The particle size of AFW also affects the recovery of PCs. For example, a reduction of black currant pomace particle size from 0.5–1 to <0.125 mm determined a 1.6–5-fold increase in PCs<sup>[20]</sup>. Particle size reduction prior to drying also affected the content in phenolic compounds in waste from carrots and white cabbage<sup>[7]</sup>. As to carrot residues, the chopping ( $\leq$ 10 mm) and grinding ( $\leq$ 5 mm) pre-treatments did not significantly influence the bioactive molecule content, while chopped samples of white cabbage residue better preserved the phenolic compounds.

#### 2.2. Extraction Methods

Novel environmental-friendly methods, including ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and supercritical fluid extraction (SFE), have been developed for sustainable recovery of PCs from AFW<sup>[21][22]</sup>. In addition, a new generation of sustainable solvents (i.e., deep eutectic solvents, DES) has been used.

UAE is based on the application of ultrasounds, which promote a greater diffusion of solvent into cellular materials, and thus improve mass transfer and cell wall disruption, so as to facilitate the release of bioactive components<sup>[22]</sup>. UAE prevents temperature increase and thermal degradation of bioactive compounds. It also allows a reduction of the extraction time, using lower quantities of solvent, cutting process costs, and benefiting from high-level automation<sup>[23][24]</sup>. UAE has been applied to the extraction of PCs from waste of the winemaking industry: anthocyanins from red grape pomace<sup>[25][26]</sup> and wine lees<sup>[27]</sup>, trans-resveratrol from red grape waste<sup>[28]</sup>, and polyphenols from red grape pomace<sup>[25][29]</sup>. As regards the supply chain of fruit and vegetables, UAE was applied to recover PCs from apple<sup>[30]</sup>, *Vaccinium* berry<sup>[31]</sup>, citrus<sup>[29][32][33]</sup>, tomato<sup>[34]</sup>, and onion wastes<sup>[35]</sup>. PCs were extracted by UAE also from olive waste (e.g., cake, leaves)<sup>[29]</sup>

<sup>[34]</sup>. The application of UAE to extraction of PCs from root and tuber wastes (e.g., potato peels), and (black) carrot pomace was also reported<sup>[36][37]</sup>. Among cereals and legumes, polyphenolic compounds were recovered by UAE from wheat bran<sup>[29]</sup> and mung bean hulls<sup>[38]</sup>.

MAE is an extraction technique combining microwave and traditional solvent extraction. The principle that MAE is based on is dielectric heating, which consists in microwave electromagnetic radiation heating a dielectric material by molecular dipole rotation of the polar components present in the matrix<sup>[21]</sup>. Shorter extraction time, higher extraction rate, minor solvent requirements, higher selectivity towards added-value compounds, and lower costs over traditional extraction methods are some of the advantages that make MAE a favorable method in the extraction of bioactive compounds<sup>[22][23]</sup> [21]. MAE has so far been used to recover different classes of PCs. Anthocyanins were recovered from grape juice<sup>[39]</sup>, red grape<sup>[26]</sup>, and black carrot wastes<sup>[40]</sup>. Polyphenols were extracted by MAE from red grape pomace<sup>[26]</sup> and red wine lees<sup>[41]</sup>. Flavonols were obtained from red grape waste. Hydroxytyrosol was recovered by MAE from olive pomace<sup>[42]</sup>.

SFE is based on the use of fluids at pressure and temperature values above or near their critical points. In particular, SFE uses renewable solvents, such as  $CO_2$ , and offers some advantages, such as easy recovery, selectivity, compound stability, reduced time, and an overall total energy saving. Apart from the unnecessity of solvent removal from the final product, the degradation process of bioactive compounds is also lower because of light and air absence<sup>[43]</sup>. SFE is especially suitable to recover extracts from solid matrices<sup>[22][23][21]</sup>. It has been applied to extract PCs from pomace of grape, apple, and orange<sup>[43][44][45]</sup> and from black walnut husks and hazelnut waste<sup>[43][46]</sup>.

DES extraction is one more analytical approach to recover PCs from AFW. DESs are prepared by mixing two or more components (e.g., hydrogen bond acceptors or hydrogen bond donors) able to interact by hydrogen bonds. Compounds used for DES preparation comprise choline chloride, DL-malic acid, citric acid, glycerol, D-(+)-glucose, D-(-)-fructose, sucrose, D-(+)-galactose, D-(+)-maltose, maltitol, and D-(-)-ribose. DES exhibit the same extraction properties than organic solvents but have negligible environmental and economic impact. Moreover, they have a GRAS (generally recognized as safe) status. They have been applied to the extraction of several classes of PCs from grape waste: phenolic acids from grape skins and red grape pomace<sup>[47][48]</sup>; anthocyanin pigment derivatives from grape waste<sup>[27][47][48]</sup>, and flavonol glycosides from red grape pomace<sup>[27]</sup>. DES were also used to extract PCs from onion waste<sup>[34][49]</sup>. Natural DES have been applied to extract polyphenols from olive pomace, in combination with homogenization, microwaves, ultrasounds, and high hydrostatic pressure<sup>[50]</sup>, and from olive leaves, kernels, and cake<sup>[34][51][52]</sup>.

#### 2.3. Fermentation and Enzymatic Treatments

Bioprocesses, such as fermentation and enzyme technology, are further approaches for the transformation of AFW into value-added products.

Solid-state fermentation (SSF) and sub-merged fermentation have mostly been used<sup>[53]</sup>. SSF by *Rhizopus oligosporus* and *Aspergillus niger* was applied to apricot pomace. The use of *R. oligosporus* as a starter determined an increase in the total phenolic content (TPC) by 70% and in the total flavonoid content (TFC) by 38%. SSF by *A. niger* increased TPC by more than 30% and TFC by  $12\%^{[54]}$ . SSF with *A. niger* was also applied to pomace from black and dwarf elderberries, and an increase in extractable phenolics by 11.11% and 18.82% was observed, respectively<sup>[55]</sup>. SSF was also applied to grape pomace, and the production of xylanase allowed the release of PCs from the substrate<sup>[56]</sup>.

As regards the application of SSF to cereal by-products, *A. niger* was used to ferment wheat bran, and higher PC content was obtained thanks to the activity of  $\beta$ -glucosidase enzymes<sup>[56]</sup>. Wheat bran was also fermented by a strain of *Aspergillus oryzae* and the TPC of ethanolic and methanolic extracts was higher in fermented samples than in the non-fermented ones<sup>[57]</sup>. The application of a strain of *Lactobacillus brevis* and *Candida humilis* to wheat bran enabled the release of PCs, thanks to the activity of cell wall-degrading enzymes<sup>[58]</sup>.

Enzyme-assisted extraction (EAE) of PCs from AFW has also been reported<sup>[21]</sup>. It is based on the ability of enzymes, such as cellulase,  $\beta$ -glucosidase, xylanase,  $\beta$ -gluconase, and pectinase, to degrade cell wall structure and depolymerize plant cell wall polysaccharides, so as to prompt the release of bound compounds<sup>[59]</sup>. The specificity of enzymes for their substrate also determines an increase in the bioactivity of extracts, thanks to the hydrolysis of high-molecular-weight compounds to a lower molecular weight<sup>[60]</sup>. The use of water as a solvent in EAE, instead of organic chemicals, also makes EAE an eco-friendly technology for extraction of bioactive compounds. Applications of EAE to extraction of PCs from grape waste, pistachio green hulls, and pomegranate peels have been reported<sup>[61][62][63]</sup>.

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