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Food Wastes as Valuable Sources of Bioactive Molecules

Sonia A. Socaci, Anca C. Fărcaș, Dan C. Vodnar and Maria Tofană

Abstract

Food industry produces worldwide millions of tons of plant-derived wastes which can be exploited as sources of high-value components: proteins, fibres, polysaccharides, flavour compounds or different phytochemicals. These bioactive compounds can be valorised as functional ingredients in food, pharmaceutical, health care, cosmetic and other products. Using the recovered bioactive molecules as functional ingredients represents a sustainable alternative of food wastes exploitation as inexpensive source of valuable compounds, while developing innovative food and non-food products with health-promoting benefits and at the same time contributing to an efficient waste reduction management. This chapter gives an overview of the main classes of bioactive compounds recovered from food wastes and their potential applications as functional chemicals, without being exhaustive.

Keywords: bioactive compounds, functional ingredients, food waste exploitation, renewable resources, recovered biomolecules

1. Introduction

Large amounts of wastes are generated annually by the food industry, their efficient management and valorisation representing one of the main objectives of European Union (EU) actions against food waste and towards sustainable development [1, 2]. The Waste Framework Directive [3] emphasised the importance of prevention of waste generation and the exploitation of wastes by reuse and recycling. Thus, in the ‘bioeconomy’ concept, the possibilities of conversion of renewable biological resources into economically viable products are addressed. In 2014, the European Commission provided the definition for the term ‘food waste’ as ‘food (including inedible parts) lost from the food supply chain, not including food diverted to material uses such as bio-based...
products, animal feed, or sent for re-distribution’ [4]. The processing by-products are also included among food waste, if these are not used for other high-value functions (e.g. animal feed and industrial uses). In this chapter, we address only the exploitation of plant-derived by-products as sources of bioactive compounds.

Until few decades ago, food wastes, if not discarded into environment, were mainly used as animal feed. Nowadays, this attitude towards wastes changed, especially due to the growing interest in protecting the environment but also due to the increasing awareness of the benefits deriving from their exploitation. The by-products resulted from the processing of raw vegetables contain sometimes appreciable amounts of bioactive compounds such as proteins, dietary fibres, polysaccharides, fatty acids, flavour compounds and phytochemicals (e.g. polyphenols) that can be extracted, purified, concentrated and reused as functional ingredients in food industry or other related sectors (e.g. pharmaceuticals, cosmetics and health-care products) [5, 6].

2. Bioactive compounds recovered from plant-derived wastes and their potential applications

2.1. General overview

The wastes generated from the food industry can be separated into two main categories: plant-derived wastes and animal-derived wastes. The animal-derived wastes can be divided in three subcategories: (i) meat products, (ii) fish and seafood and (iii) dairy products, whereas the plant-derived wastes can be classified into four subcategories: (i) cereals (e.g. rice bran, wheat bran and brewers’ spent grain), (ii) root and tubers (e.g. potato peel, sugar beet and molasses), (iii) oil crops and pulses (e.g. sunflower seeds, soybean seed and olive pomace) and (iv) fruit and vegetables (e.g. orange peel, grape pomace, apple pomace, tomato skin and pomace) [5, 7]. We further focus only on the plant-derived wastes chemical characterisation in terms of composition and content in functional compounds. The plant-derived by-products and especially those from fruits, vegetables and oil crops processing are generated in large amounts, some of them being produced in millions of tons annually worldwide [5, 8–10]. Disposal of such quantities of waste represents a challenge and an environmental problem. Apart from being used as animal feeds or fertilisers, the research conducted in the last decades clearly showed that the by-products resulted from processing of plant materials contained valuable nutrients which could be exploited in the development and production of new functional ingredients [11–15].

There is a wide range of extraction techniques used for the isolation and purification of the bioactive compounds from plant-derived wastes, some of them being based on new emerging techniques. The development of new extraction methods as well as the optimisation of existing ones, in order to increase, for example, the extraction yield or the selectivity for a certain compound, or to improve the production of a natural bioactive compound from a waste, has seen a real upsurge in the last decade [16]. Nevertheless, there is no universal extraction
<table>
<thead>
<tr>
<th>Compound class</th>
<th>Waste origin</th>
<th>By-product source</th>
<th>Extraction techniques</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>Cereals</td>
<td>Brewers’ spent grain</td>
<td>Ultrasonic-assisted extraction</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sequential extraction of proteins and arabinoxylans</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Enzymatic-assisted extraction</td>
<td>[19]</td>
</tr>
<tr>
<td>Oil crops</td>
<td>Rapeseed meal</td>
<td></td>
<td>Ultrasound-assisted aqueous extraction</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>Sunflower meals</td>
<td></td>
<td>Alkaline solubilization and acid precipitation</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Hazelnuts meal</td>
<td></td>
<td>Solvent extraction (water, acetone)</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>Canola meals</td>
<td></td>
<td>Alkaline solubilization and acid precipitation (Isoelectric precipitation)</td>
<td>[23, 24]</td>
</tr>
<tr>
<td></td>
<td>Palm kernel cake</td>
<td></td>
<td>Electro-activated solutions (non-invasive extraction method)</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>Apricot kernel cake</td>
<td></td>
<td>Salt precipitation</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Enzymatic hydrolysis</td>
<td>[26]</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>Cereals</td>
<td>Brewers’ spent grain</td>
<td>Enzymatic hydrolysis</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sequential extraction of proteins and arabinoxylans</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acid hydrolysis</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Fruits and vegetables</td>
<td>Citrus peel and apple pomace</td>
<td>Subcritical water extraction</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Orange peel</td>
<td>Microwave extraction</td>
<td>[31]</td>
</tr>
<tr>
<td>Lipids</td>
<td>Cereals</td>
<td>Brewers’ spent grain</td>
<td>Soxhlet extraction</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>Fruit and vegetables</td>
<td>Grape seeds</td>
<td>Pressurized carbon dioxide extraction with compressed carbon dioxide as solvent and ethanol as co-solvent</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Supercritical fluid extraction</td>
<td>[34]</td>
</tr>
<tr>
<td>Polyphenols</td>
<td>Cereals</td>
<td>Brewers’ spent grain</td>
<td>Alkaline hydrolysis</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>Oil crops</td>
<td>Rapeseed</td>
<td>Ultrasound-assisted aqueous extraction</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Olive by-products</td>
<td>Continuous counter-current liquid-liquid extraction</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sunflower meals</td>
<td>Chemical (acid) hydrolysis</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>Fruits and vegetables</td>
<td>Tomato pomace and skin</td>
<td>Mild-acidic protein extraction with adsorptive removal of phenolic compounds</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potato peels and tubers</td>
<td>Enzymatic-assisted extraction/solvent extraction</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Orange peels</td>
<td>Pressurized liquid extractor</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Forest fruits pomaces</td>
<td>Solvent extraction (stirring)</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Apple pomace</td>
<td>Ultrasound extraction</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Grape seeds</td>
<td>Nanofiltration</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Fruits and vegetables</td>
<td>Tomato pomace and skin</td>
<td>Supercritical fluid extraction</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Citrus peel</td>
<td>Ultrasound extraction</td>
<td>[44]</td>
</tr>
<tr>
<td>Carotenoids</td>
<td>Fruits and vegetables</td>
<td>Sea buckthorn seeds</td>
<td>Supercritical carbon dioxide fluid extraction</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Enzymatic-assisted extraction</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>Essential oils</td>
<td>Citrus peel</td>
<td>Solvent extraction, distillation, hydrodistillation</td>
<td>[48]</td>
</tr>
</tbody>
</table>

Table 1. Examples of bioactive compounds from plant-derived wastes and the employed extraction techniques.
technique for the bioactive compounds. When an extraction technique is chosen, several criteria have to be considered, such as waste composition, aggregation state, homogeneity, and so on. Also, plant-derived waste is prone to microbial degradation, so an appropriate way of preservation is necessary for its storage and further exploitation. One of the most common and economically feasible methods used for preservation is the drying of the waste and thus reducing the water content and lowering the microbiological activity [11].

In Table 1, examples of some of the most common extraction technique for the main classes of high-value compounds and their sources are given.

2.2. Proteins

Proteins are macronutrients with an important role in human nutrition, having high nutritional value. Nowadays, the consumers are more concerned about their health and are starting to realise the tight correlation between health and diet. The trend is towards vegetarianism, and thus finding new plant sources of protein is crucial for the food industry. For a by-product to be considered as a source of protein, it has to fulfil major requirements: to have high protein content and this protein to be quality protein (well-balanced essential amino acid composition) [12]. Also, the allergic or toxic substances that may be present in the by-product must be removed prior to its utilisation as source of protein.

The main wastes with a relatively high content of protein are the defatted meals obtained from oil industry, including sunflower, canola, rapeseed, but also palm and peanuts. The defatted by-products generated from oil refineries (oil cake, stem and grain husk) are not only good sources of proteins but are also available in large quantities and at a low cost.

Sunflower proteins have been extensively evaluated as food ingredients. Sunflower seeds content in proteins ranges between 10% and 27.1% (dry weight (DW) basis), thus making the sunflower oil cake a good source of quality protein. The sunflower protein isolate's or concentrate's characteristic is the relatively high content in phenolics, compounds that may alter the proteins' functional properties and their shelf life [49]. However, the current tendency is not to obtain protein isolates free of phenolics, but to keep these compounds into the isolates due to the antioxidant activity they exert. The protein concentrates containing different concentrations of phenolics were studied and the results showed that they have high water solubility, moderate water-holding capacity, emulsifying, foaming and gelation capacity similar to commercial isolates [21].

Another source of plant protein is the canola seeds. These seeds contain two main types of storage proteins: salt-soluble (cruciferin) and water-soluble (napin), the total protein content in the defatted canola meal being around 32% [24]. The concentration of proteins in canola protein isolates, when conventional direct alkaline extraction is used, ranged between 66% and 76% [23, 24], while using salt precipitation method may increase the concentration of proteins in isolates up to 93% [24]. There are new emerging non-invasive methods, such as electro-activated solutions, that can be used for the extraction of proteins from canola meals with better extraction yields by solubilising the proteins without damaging their native conformations and maintaining their functional properties [25].
Rapeseed stem, the residual biomass remaining after the extraction of oil, represents roughly 30% of the plant and may also be considered to be used for proteins’ recovery. The protein concentration in the rapeseed stem extract, using a green solvent (water) in an enhanced ultrasound extraction, was up to 0.03 g BSA/100 g DW. The ultrasound-assisted extraction showed an increase in extractability and at the same offering the possibility of scaling up [20].

Functional proteins can also be extracted from hazelnut cake (contains up to 54.4% proteins). The isolated hazelnut meal protein was found to exert good antioxidant activity (158–461 mmol Trolox/kg), iron chelation (60.7–126.7 mmol EDTA/kg), antiproliferative activity on colon cancer cells (IC_{50}: 3.0–4.6 mg/ml) and good oil absorption (7.4–9.4 g/g) [22].

In the palm oil-producing countries (e.g. Indonesia and Malaysia), the palm kernel cake is one of the main by-products generated by food industry [26]. Palm kernel cake contains in average 15–21% crude protein, but it is deficient in lysine, methionine and tryptophan, and thus has a poor utility being usually used as feed for ruminants [50, 51]. Nevertheless, palm kernel cake is still a potential source of plant protein. The extracted protein isolates have a 68.50% protein concentration when alkaline extraction was used. Attempts in optimisation of extraction technology were carried out in order to transform the extracted protein into a bioactive plant protein (e.g. by enzymatic hydrolysis) by adding functional properties such as antioxidant function [26, 52].

Cereal origin wastes represent another potential source of bioactive molecules, including plant proteins. Brewers’ spent grain is the main insoluble residue generated by the brewing industry. This by-product results after the production of wort and it mainly consists in barley grain husks with minor fractions of pericarp and endosperm [53]. Its chemical composition is dependent on several intrinsic and extrinsic factors (barley cultivar, harvest time, type of malt used in the brewing process, mashing conditions, etc.) [54], but regardless of these factors it contains appreciable amounts of valuable compounds (proteins, lipids, carbohydrates, polyphenols and minerals) that remain unexploited in the brewing process. Brewers’ spent grain has a high content (18–35.4%, w/w) [18, 55, 56] of quality protein, with lysine accounting for 14.3% of total protein content [55]. The extraction of protein from brewers’ spent grain may be performed by classical alkaline extraction, but recently new integrated processes are developed for a more efficient exploitation of this by-product. For example, simultaneous extraction of proteins and arabinoxylans by use of alkaline reagents directly from brewers’ spent grain without any pre-treatment [18] has a great potential to be scaled up being an innovative environmental friendly process that allows the recycling of the reagents and at the same time saving 93% in costs [57]. The incorporation of chitosan into the brewers’ spent grain protein had as result a composite film with antimicrobial and antioxidant activities which can be used in packaging materials for foods [58].

The apricot kernel press cake, the waste remaining after the oil extraction, contains 34.5% crude protein which may be valorised by as protein isolates. In this case, before the alkaline extraction of proteins, a pre-step of detoxification is required in order to remove the HCN present in the kernel cake. The obtained isolates had a protein concentration of 68.8% and fairly good functional properties, especially water and oil absorption capacity and foaming properties [27].
The proteins recovered from plant-derived wastes have several functional properties when incorporated in food products: emulsifying agents, film-forming properties, flavour binding, viscosity increase by binding the water and gelation properties. The recovered proteins are successfully used for food fortification, especially in meat and milk products, infant formulae, bakery products and pasta products [20, 22, 27, 59].

2.3. Polysaccharides

Polysaccharides are widely distributed in nature, with about 99% being located in plants and vegetables, the representative ones including starch, cellulose, hemicelluloses, pectin and inulin [60]. These compounds are also referred to as dietary fibre and can be divided into two categories based on their water solubility [61]:

1. insoluble dietary fibre—are insoluble in water and resistant to hydrolysis by digestive tract enzymes (cellulose, hemicelluloses, lignin—non-carbohydrate compounds);
2. soluble dietary fibres are soluble in water and well fermented by digestive tract enzymes (pectin, inulin, gums and mucilages).

In plants, polysaccharides have important functional roles: maintaining the living cell structure, and water binding or energy suppliers. These properties are exploited by the food industry and other related fields in the development of new food additives, functional ingredients or materials for bioactive molecules delivery and controlled release. Their suitability for pharmaceutical or medicinal uses is due to their innocuousness, biocompatibility, biodegradability and water solubility. Thus, there is an increasing and constant interest in finding new sources of plant-derived polysaccharides—the bioagro-waste streams being very promising in this sense [60, 62].

The fruit- and vegetable-processing sector produces wastes (peels, pulp and seeds) that are rich, low cost and sustainable sources of polysaccharides. After isolation and purification, the recovered polysaccharides may have manifold applications.

Pectin is a polysaccharide with a heterogeneous structure that depends on the plant origin, the part of the plant where it is located (peels, pulp, seed, etc.) and how it is extracted. The ‘building block’ is the uronic acid residue link through α-1-4-glycosidic bonds, forming a galacturonyl polymer backbone. The structural diversity of pectin provides a wide range of physico-chemical and functional properties (gelling, emulsifier, thickening agents, film-forming, water-holding, prebiotic activities, etc.) essential for food industry. According to the Joint Food and Agriculture Organization/World Health Organization (FAO/WHO) Expert Committee on Food Additives and the European Commission, a pectic polysaccharide must have a content of minimum 65% in galacturonic acid [60–63]. Wastes such as orange peels or apple pomace are well-known sources of pectins, but there are also other waste streams that can be exploited in this sense. The pectins from 26 vegetable wastes were characterised in a very complex study, in the framework of EU project NOSHAN, including orange peel, onion hulls, parsley, endive roots and leaves, leek leaves, fresh cabbage, pea pod, sugar beet flakes, berries, apple pomace, sea buckthorn pulp, hop, olive pomace, tomato skin, grape pomace, whole pear and shabal. The results showed that the structure of the pectin extracted from wastes is similar to that from...
the raw matrices, although the methylation and acetylation degrees are lower due to the processing and/or enzymatic actions. The collected data also emphasise the potential of the recovered pectin to be used either as food additives or other applications (if the minimum concentration in galacturonic acid is not reached) [63].

The most important sources of soluble dietary fibres are the wastes derived from citrus fruits processing. The pectin content differs considerably among citrus varieties, but it generally ranges between 20% and 30% of citrus peel dry weight. Cellulose and hemicellulose can also be recovered from citrus waste as it comprises approximately 50–60% of citrus peel weight. The dietary fibres are not only present in high amount in citrus peels but also have important features due to the presence of associated bioactive constituents (flavonoids and vitamin C) with antioxidant properties, which may provide additional health-promoting effects [64, 65]. For example, the pectin extracted from citrus peel and apple pomace by subcritical water extraction (with maximum yields of 22 and 17%, respectively) showed a high antioxidative and anti-tumour activity [30]. Soluble dietary fibres also reduce the intestinal absorption of blood cholesterol, whereas insoluble dietary fibre associates to water absorption and intestinal regulation apart from the well-known probiotic and health benefits [66].

As previously mentioned, brewers’ spent grain besides being a source of quality plant protein is also a good source of carbohydrates, their level being up to 50% of the by-product weight [28]. The main carbohydrates in brewers’ spent grain are cellulose (~17% dw) [13, 18, 32] and hemicelluloses, mainly arabinoxylan (25–28% dw) [13, 18]. The vegetable matrices being rich in hemicelluloses can be hydrolysed (e.g. with diluted acid) in order to release the monosaccharides (xylose and arabinose) which can be further subjected to a fermentation process to generate valuable products (e.g. xylitol, a sweetener used in food industry) [29]. Arabinoxylans are considered dietary fibres with a broad range of potential uses as functional ingredients in food products. Their extraction from brewers’ spent grain may be performed under strong alkali conditions and also by using an innovative fully integrated process that sequentially extracts the proteins and arabinoxylans [18].

2.4. Phenolics

Phenolics are among the most studied phytochemicals in the last decades. The interest showed by the scientific community in finding new and unconventional sources of phenolic compounds is due to the many studies that suggested that there is an association between the consumption of diets rich in phenolic compounds and a reduced risk of cardiovascular and neurodegenerative diseases [37, 66, 67]. Also, the recovery of phenolic compounds from food processing by-products and their use as functional ingredients sustain the increasing efforts for a sustainable food production.

During fruit processing, the beverage industry leaves between 25 and 35% mass of the raw material called fruit pomace. Unfortunately, some part of pomace in the fruit industry still goes to landfill, and causes environmental pollution and huge losses of valuable materials which could be exploited as a great variety of natural additives and many health-promoting ingredients (phenolic compounds, vitamins, carotenoids and dietary fibre) [68, 69]. Phenolic compounds of different plant sources such as grape and apple pomace are known as potent
antioxidants and radical scavengers. The wine-making industries produce millions of tons of residues (grape pomace), which represents a management issue from both ecological and economical point of view [70]. Grape pomace is a phenolic-rich dietary fibre matrix that combines the benefits of both fibre and antioxidants in the prevention of cancer and cardiovascular diseases [66]. Moreover, the grape seeds are considered to be a disposable waste material by the majority of wineries. They are usually discarded, burned or used as animal feed [45]. The oil extracted from the grape seed offers a wide range of benefits for human health, due to its high content of unsaturated fatty acids and antioxidant compounds such as monomeric flavan-3-ols, phenolic acids and oligomeric proanthocyanidins, which is the reason why the valorisation of this by-product is of great interest. Crude grape seed oil consists mainly of linoleic and oleic unsaturated fatty acids and also of palmitic and stearic saturated fatty acids [33, 34]. A study regarding the chemical characterisation of the grape seed extracts obtained by supercritical CO₂ extraction showed that their content in trans-resveratrol was similar to the contents reported in the literature for red wines. This demonstrates that a considerable amount of trans-resveratrol remains unexploited in grape seeds after the fermentation process [33]. An alternative of reuse of grape seeds is as flour incorporated in food products. For example, formulations of frankfurters with grape seed flour showed a decrease in oxidation processes (due to the strong antioxidant activity of the flour), increased total dietary fibre content and water-holding capacity of the final product [59], while the addition of apple pomace extract in meat products reduces the number of synthetic antioxidants needed to be added, and increases the health-promoting properties of the finished product [68].

Besides being a serious environmental problem, olive by-products can also represent a precious resource of potentially valuable molecules. It is worth mentioning that 98% of olive fruit phenols are lost during oil extraction. These compounds are distributed between the olive mill wastewaters (OMWs) phase (approximately 53%) and the solid phase—the ‘pomace’ (approximately 45%). Consequently, only a 2% fraction of the phenolic classes remains the oil phase depending on the extraction system and olive variety [71]. The evidence relating to decreased prevalence of chronic heart diseases, atherosclerosis or other diseases caused by oxidative stress, through a Mediterranean diet, has oriented scientific research towards the best use of olive-processing by-products (olive leaves and olive mill wastewaters) in order to produce purified natural antioxidants or high antioxidant-rich preparations that could be incorporated in foods, cosmetics and pharmaceuticals [37, 67]. The studies on chemical constituents of olive leaves revealed that phenolic compounds stand out as predominant micronutrients, hydroxytyrosol and oleuropein considered as majority [72]. For example, the hydroxytyrosol-rich olive leaf extract had an inhibitory activity against breast cancer cell proliferation [37]. Also, phenolic-rich extract from OMW and hydroxytyrosol and oleuropein extracts from olive leaves had very pronounced hypocholesterolaemic effects, hypoglycaemic effect, protective action against lipid peroxidation and enhanced antioxidant defence system [73, 74].

Sunflower seeds contain high amounts of polyphenols such as caffeoylquinic and caffeic acids, accounting up to 4% dw. Among all, 5-O-cafeoylquinic acid (chlorogenic acid) is the predominant compound. To achieve sustainability of sunflower processing and complete utilisation
of by-products arising from sunflower oil production, polyphenols co-extracted during sunflower protein recovery from the expeller were recovered by adsorption technology. In addition, an integrated process was optimised in order to enhance the recovery of polyphenolics as by-products of protein production from sunflower press cake [38, 75].

Other unconventional source of phenolic compounds is the potato peels. Phenolic acids are the most abundant phenolic compounds in potatoes peels, the main representative being the chlorogenic acid (up to 95–98% of phenolic compounds) [39, 76]. It is present in the form of three main isomers: chlorogenic acid (3-O-caffeoylquinic acid), neochlorogenic acid (3-O-cafeoylquinic acid) and cryptochlorogenic acid (4-O-cafeoylquinic acid) [76]. Its extraction from potato peels may be performed by conventional solvent extraction [40], ultrasound-assisted extraction [41] or using an optimised solvent extraction using pressurised liquid extractor [39]. The optimisation of an extraction method is a crucial step for researchers to accurately quantify the content in phenolic compounds and also to be able to estimate their potential health benefits when incorporated in food as functional ingredients. The extracted quantity of phenolic acids from potato peels depends not only on the method parameters but also on genetic factors. While the total phenolics content varies between cultivars and geographical regions, the most abounding isomer of chlorogenic acid was in all cases the 5-O-cafeoylquinic acid [39, 40].

### 2.5. Carotenoids

Carotenoid compounds are known for their health-promoting effects, especially due to their high free radical-scavenging activity. Being powerful antioxidants, when ingested they protect the human body from the damaging actions of the reactive oxygen species and thus lowering the risk of several chronic diseases (cardiovascular diseases, diabetes and cancer). They are fat-soluble pigments which are responsible for the bright-yellow colour of many fruits and vegetables [77].

Lycopene is the main carotenoid found in tomatoes. Some studies suggested that a direct correlation may be established between the consumption of foods rich in lycopene and a low risk of prostate cancer [78].

Tomato (*Solanum lycopersicum* L.) is the second-most consumed vegetable in the world [79]. The solid by-products resulted from its processing into food products such as tomato juice, paste, puree, ketchup and sauce reaching up to 50,000 tons per year [16]. Their exploitation as a source of carotenoids (mainly lycopene) may provide economic benefits. Several techniques are used for the extraction of lycopene from tomato by-products of which enzymatic-assisted process is a promising one. When enzymatic method is used, the tomato by-products are pretreated by crude enzyme extracts with pectinolytic, cellulolytic and cutinolytic activities prior to their conventional solvent extraction. The results showed an enhancement in the extraction of lycopene from tomato by-products (2.7 mg/100 g) and also a higher overall antioxidant activity for the enzymatic extract (even higher than that of BHA) compared to the one obtained by conventional ethanol extraction [16].
In general, bioaccessibility of carotenoids is low. However, in some fruits, such as mango and papaya, they are present in oil droplet in an esterified form with fatty acids. This kind of structure enhances their extraction and bioavailability during digestion [80]. Poor postharvest technology is one of the major inconveniences in mango annual production, accounting for nearly 60–80% of losses. Therefore, processing mango into flour represents a viable alternative for its use as a functional ingredient and to reduce wastage. The carotenoid content of mango flours ranged from 56.46 to 160.64 μg/g and was found to be higher in ripe mango flours than in green mango flours. In addition, the flour processed from the mango peel has been found to contain significant superior qualities than that from mango pulp in terms of total phenolic, anthocyanins, flavonoids and vitamin C contents and antioxidant activities [81].

Citrus waste is voluminous, heterogeneous, chemically complex and highly biodegradable; therefore, it cannot be disposed of in a landfill without a previous valorisation, in order to avoid both economic loss and environmental pollution issues. About 40–50% of the quantity of this fruit is processed for juice and marmalade production and approximately 50–60% w/w of the processed fruit becomes waste. This by-product contains a wide range of bioactive compounds, such as essential oils, carotenoids, fibre, hesperidin and limonin, which have many applications in food, cosmetic and pharmaceutical industry. After the production of orange juice, the remaining outer layer called flavedo contains considerable amounts of the natural carotenoids. These bioactive compounds comprise approximately 0.1–0.5% of citrus peel dry weight. The major carotenoids available in citrus are α- and β-carotene, lutein, zeaxanthin and β-cryptoxanthin, which are known to be responsible for a wide range of functional properties, mainly offering protection against the reactive oxygen species damaging actions at the cellular level [64, 82–84].

2.6. Other compounds

The wastes from fruits and vegetables can be exploited by microbial processing in order to obtain valuable enzymes such as amylolytic enzymes from banana waste, mango kernels; pectinolytic enzymes from orange peel, lemon peel; tannase from grape seeds; protease from mango peel, potato peel; lipase from coconut cake, lemon peel; and invertase from orange peel, banana peel. The microbial treatment can also be used for the production of organic acids, including lactic acid, citric acid, succinic acid and acetic acid from wastes of potatoes, banana, mango, apple, pineapple and many others [85]. These valuable chemicals can be further exploited as raw materials for other processes or as functional ingredients for newly developed food products and so on [86]. Another example of valuable products recovered from fruit wastes, more exactly, from citrus fruits peels (orange, mandarin, lime, lemons, etc.), is the essential oils. Citrus essential oils extracted from the peels discarded after the fruits processing can be valorised: as flavouring agents in different food products (e.g. soft drinks and confectioneries), perfumes, personal care products, household products; in food preservation enhancing the product’s shelf life due to their antioxidant and antimicrobial properties, and thus representing an attractive alternative to synthetic antioxidants and preservatives; and as functional chemicals in agriculture as insects repellent and other more uses [48, 87–89].
3. Conclusion

Food wastes are renewable resources of high-value extractable or convertible chemicals which can be exploited for the development of new functional ingredients, respectively, for the generation of bio-fuels. The scientific research is focused on finding new ways of valorisation of food industry by-products by identifying or optimising the most appropriate extraction methods for the recovery of the biomolecules, as well as by strengthening the cooperation with food industry partners in implementing adequate solutions for a sustainable development and increased competitiveness.

The ‘zero-waste’ desiderate can be reached by reusing the high-value compounds from by-products in innovative and unconventional ways which may generate profits in a sustainable food production system. The recovered biomolecules are also of great interest for pharmaceutical industry (e.g. carrier agents and controlled release), cosmetics, agriculture, chemical industry and so on.

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