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Chapter 1

Antioxidant Compounds Recovered from Food Wastes

Sonia Ancuța Socaci, Dumitrița Olivia Rugină, Zorița Maria Diaconeasa, Oana Lelia Pop, Anca Corina Fărcaș, Adriana Păucean, Maria Tofană and Adela Pintea

Additional information is available at the end of the chapter

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Abstract

The increase awareness of nowadays consumers regarding the food they purchase and consume and the health has led to an increase demand of foods containing biologically active compounds, namely antioxidants, which can help the body to fight against oxidative stress. As a consequence finding, new or nonconventional sources of antioxidants are a priority for food and also pharmaceutical industries. Wastes from fruits and vegetable processing are shown to contained valuable molecules (antioxidants, dietary fibers, proteins, natural colorants, aroma compounds, etc.) which can be extracted, purified and valorized in value-added products. The present chapter is underlying the great potential of food wastes to be exploited as sources of antioxidants based on the scientific evidences regarding the possibilities of extraction and purification, health benefits and envisaged applications of antioxidants recovered from these wastes.

Keywords: bioactive compounds, antioxidants, food waste exploitation, functional ingredients, health benefits

1. Introduction

Statistics announced by the Food and Agriculture Organization (FAO) of United Nation showed that approximately one-third of food produced for human consumption is wasted globally. These statistics indicated that even though the quantity of wastes differs between regions, all regions have major losses at production level. Fruits and vegetables, plus roots and tubers, have the highest wastage rates of any food. The same organization reported
that a global quantitative loss and waste of root crops, fruits and vegetables per year is 40–50% [1]. The disposal of such amounts of wastes not only represents a challenge for the food processors, but it is a matter of crucial importance at international level due to both environmental pollution and economical aspects [2, 3]. Studies showed that plant-derived wastes should be reconsidered and regarded as renewable sources of valuable molecules which can be extracted, purified and valorized in different fields, including food industry, cosmetics, pharmaceutical and chemical industry and so on [4, 5]. For example, the search for efficient and nontoxic natural compounds with antioxidant activity has gained increased attention, especially due to the consumers’ awareness regarding the direct relation between food (diet) and health [6]. The introduction into the diet of the antioxidant compounds, like polyphenols, is an efficient way to combat the negative effects caused by the excess of reactive oxygen species (ROS) in the body. The oxidative stress, caused by the ROS, is considered to be one of the main triggers of chronic diseases, such as cancer, diabetes, cardiovascular or neurodegenerative disorders [7]. In the case of fruits and vegetables, usually a high amount of antioxidant compounds is found in peels, kernels or seeds, namely in parts that are removed during processing and become wastes [8–13]. Thus, these compounds could be extracted from fruit and vegetable wastes and reused in other food products, as functional ingredients able to confer some characteristic quality criteria and at the same time to exert human health benefits due to their antioxidant properties.

The aim of this chapter is to emphasize existing studies on fruit and vegetable wastes regarding their potential as sources of bioactive compounds (antioxidants) with health-promoting benefits that can be exploited as functional ingredients.

2. Extraction and identification of antioxidants from food wastes

Nowadays, the growing interest of consumers toward the relation between the ingested food and the effects on health has led to an increase demand of foods without what they perceive harmful chemicals (e.g., synthetic preservatives, antioxidants, colorants) and with high nutritional and functional properties. This demand, in the scientific field, was translated by intensifying the research focused on finding new sources of bioactive molecules (antioxidants), optimizing the extraction and purification methods as well as developing innovative functional foods that promote health. In this conjuncture, the exploitation of food wastes (by-products) for the recovery and reuse of valuable bioactive compounds is one of the most sustainable approaches. Thus, efficient extraction techniques can be implemented for the separation and isolation of naturally occurring compounds with antioxidant characteristics from food wastes, such as polyphenols, carotenoids, glucosinolates, dietary fibers and so on.

There is no universal method for the extraction of bioactive compounds, but in order for a method to be suitable it has to fulfil several requirements, including selectivity toward the analyte, high extraction yields, possibility of solvent recovery (e.g., environmental
friendly) or using “green solvents,” maintaining the functionality of the recovered molecules, low-cost reagents, possibility to be implemented from laboratory scale to industrial scale and so on [14–17]. Among the classical methods used for the isolation of bioactive compounds, the most common ones are solid-liquid extraction (maceration), Soxhlet extraction and liquid-liquid extraction [18]. Depending on the type of matrix (fruit and vegetable waste) and on the type of compounds that are to be recovered, solvents with different polarities may be used (e.g., methanol, ethanol, methanol-water mixtures, water, acetone, ethyl-acetate and so on) [16, 19–21]. In the case of phenolic compounds such as flavonoids or proanthocyanidins (condensed tannins), improved extraction yields were noticed when the organic solvent was used in combination with water, while for the methoxylated compounds recovered from mango peels, a higher yield was achieved when less polar solvents such as acetone were used [16, 22]. Choosing the appropriate extraction solvent is of utmost importance, because it significantly influences the yield and the composition of the extract. Nevertheless, the enhancement of the extraction procedure may be also achieved by optimizing the sample-to-solvent ratio, extraction temperature and time, agitation degree and particle size [18, 23, 24]. Although conventional methods were optimized, there are still some limitations in their use mainly due to the high amount of solvent, time-consuming, difficulty to scaled-up. Thus, to overcome these limitations and in accordance with the “zero waste” desiderate, the current researches are focused on developing greener, sustainable and viable extraction processes. The modern extraction techniques comprise microwave-assisted extraction, ultrasound-assisted extraction, pressurized liquid extraction (e.g., pressurized hot water extraction), enzyme-assisted extraction, supercritical CO2-based extraction and other emerging techniques [18, 25–27]. For maximum valorization, several integrated extraction systems were developed (e.g., biorefineries), in which the wastes are subjected to sequential extraction steps for the recovery of different classes of bioactive compounds which can be further used such as or as raw materials for value-added chemicals production [17, 28, 29]. Recently, a new integrated extraction-adsorption process has been developed for production of large quantities of extracts rich in antioxidants. This process was proposed for a selective recovery of antioxidants from black chokeberry wastes at pilot scale, by applying a scale-up factor of 50, but the results were similar to those obtained at laboratory scale [30].

The identification and quantification of the recovered antioxidant compounds are generally achieved using high-pressure liquid chromatography (HPLC) and hyphenated techniques (e.g., LC-MS), in particular spectrophotometric methods (e.g., UV-VIS). The bioactivities of the antioxidant compounds are evaluated using methods for the assessment of their antioxidative activity (2,2-diphenyl-1-picrylhydrazyl (DPPH), ferric reducing antioxidant power (FRAP), 2,2’-azino-bis 3-ethylbenzothiazoline-6-sulphonic acid (ABTS), cupric reducing antioxidant capacity (CUPRAC), Oxygen radical absorbance capacity (ORAC)), inhibition of lipid oxidation (peroxide value, Thiobarbituric acid reactive substances (TBARS)), antimicrobial activity, antiproliferative activity and so on. Table 1 summarizes some of the techniques generally used for the separation and isolation of antioxidant compounds as well as the analytical methods applied for their bioactivity evaluation.
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Table 1. Some techniques used for the separation and isolation of antioxidant compounds and the analytical methods applied for their bioactivity evaluation.
3. Potential health benefits of recovered antioxidants

3.1. Berries

Blueberries, ribes, chokeberries, raspberries, and blackberries are used to obtain food products such as juices, jams, and jellies. A high amount of wastes are released during industry manufacturing of these fruits. Hence, valuable compounds from wastes, such as anthocyanins, phenolic acids, and flavonoids, could be successfully recovered and used for different industries.

Seed pomace, wastes of blackberry (Rubusfruticosus L.) and raspberry (Rubusidaeus L.), is generated in large quantities, being a good raw material for oil extraction. Besides linoleic (omega-6) and α-linolenic (omega-3) (2–4:1 ratio) content, these oils are also rich in bioactive compounds, such as tocopherols, phenols, sterols, and carotenoids, which are known to exert antioxidant properties. Therefore, the composition of the oil resulted from blackberry and raspberry seed pomace proved to be stable despite a long-term frozen, due to the presence of natural antioxidants [42]. Consequently, these seed oils can be considered value-added products and could be used as functional or nutraceutical food products.

Leaves could also be a potential source of health-promoting compounds. Leaves and pomace of cranberry (Vacciniummacarpon L.) contained more polyphenols and exhibited higher antioxidant activity than fruit and juices. Therefore, leaves and pomace could be another excellent source for the production of foods with high health-promoting value [43].

Among polyphenols, anthocyanins and ellagitannins from berries are known for their antitumor potential [44, 45]. A waste of black raspberry seeds applied on colon cancer HT-29 cells inhibited cellular proliferation and induced apoptosis, both through the extrinsic apoptotic pathway (activation of caspase 3, 8) and through intrinsic apoptotic pathway (activation of caspase 9 and poly(ADP-ribose) polymerase (PARP)) [46].

3.2. Apples

The apple waste generally refers to a heterogeneous mixture of peels, pomace, and seeds. Apple waste resulted after juice processing was tested on tumor colon HT29, HT115, and CaCo-2 cell lines. Results showed that waste compounds are able to confer protection against DNA damage, to improve barrier function and to inhibit cell invasion [47]. Comparing the inhibitory effects of nonextractable antioxidants with extractable antioxidants from a freeze-dried apple waste on HeLa, HepG2, and HT-29 human cancer cells, the nonextractable antioxidants were more efficient [48].

Apple peel waste could also be an excellent source of natural antioxidants and bioactive compounds that may improve the human health [49]. Apple peel extract showed a significant dose response reduction in cell proliferation in the HT-29 colon cancer cells but not on MCF-7 breast cancer cells, from ten different extracts of fruits and berries which have been tested [50].
3.3. Citrus

The production of citrus fruits, the most widely cultivated fruits, is increasing every year due to a high market demand. Orange is the main citrus fruit that dominates the global customer requests. Unfortunately, 50–60% of the fruits including seed, peel and segment membrane resulted from juice production ends up as waste [51]. Among these wastes, citrus peel is the major constituent accounting 50% of the wet fruit mass. It contains flavonoids, carotenoids, polyphenols, ascorbic acids, pectin, dietary fibers and essential oils [52]. Orange (Citrus aurantiun) flesh waste has a higher antioxidant activity than the peel. Although both of the extracts used in a study on human leukocytes showed protection against H$_2$O$_2$-induced DNA damage [53].

3.4. Exotic fruits

Pomegranate fruit gained a lot of interest due to multiple beneficial effects on human health. A recent study demonstrated that the antioxidant potential of pomegranate extract is directly related to the phenolic content, whereas its antiproliferative activity is mainly attributed to ellagic acid [54]. The ability of ellagitanins from Punica granatum L. to reduce breast MCF-7 and prostate LNCaP cancer cell proliferation was proved [55].

Juice industry underuses large amounts of passion fruit residues. The seeds of passion fruit are used for oil production, but the residue remained after the seed cold pressing (cake seed) still contains compounds of interest, like fatty acids and/or others polyphenols. Certainly, the antioxidant and the antimicrobial activities of passion fruit residue contribute to its adding value [56]. Similarly, the wastes of mango, peel and kernel contain a noteworthy amount of bioactive components such as xanthones (mangiferin), flavonoids, flavanols, and phenolic acids with therapeutic effects [57]. The Antidesma thwaitesianum Müll. Arg. fruit waste was tested on six human normal and cancer (COR-L23, A549, LS174T, PC-3, MCF7 and HeLa) cell lines. Interesting is that extracts of fresh fruits exhibited moderate cytotoxicity against human breast MCF7 cells, while the extract obtained by decocting the residue left after maceration of dried fruits showed the highest cytotoxicity on COR-L23 carcinoma lung cells [58]. The waste resulted from Myracrodruon urundeuva seeds, containing steroids, alkaloids and phenols, was twofold more cytotoxic on leukemia HL-60 line than on glioblastoma SF-295 and Sarcoma 180 cells [59]. All these data are strong evidence that exotic fruits wastes are a valuable source of antioxidants with potential health benefits.

3.5. Potatoes and tomatoes

Industrialization of potatoes and tomatoes generates by-products rich in antioxidants. There are scientific evidences that wastes of potatoes and tomatoes could be used as natural antioxidant additives in the protection of vegetable oils, effectively limiting the oxidation of oils [60, 61]. The main antioxidant compounds that have been identified in potato waste were caffeic acid, chlorogenic acid, protocatechuic acid, para-hydroxybenzoic acid and gallic acid [62]. The antioxidant and antiproliferative activity of tomato waste were strongly correlated with its concentration in β-carotene and lycopene [63]. The waste obtained during the production
of tomato juice scavenged hydroxyl and superoxide anion radicals and exerted anticancer properties, by inhibiting HeLa, MCF7 and MRC-5 tumor cell growth [64].

4. Applications of recovered antioxidants

Fruits, vegetables, and plant-derived wastes are commonly composed of peels, stems, seeds, kernels, shells, bran, and trimmings residues being a promising source of functional compounds due to their favorable nutritional and rheological properties. The most important bioactive compounds found in these types of wastes are fibers, phenolic compounds, vitamin E, C, carotenoids, and other antioxidants, which are found to have beneficial effects for human health. Trying to comply with the consumers’ demand for healthier products, the modern food industry is presently focused on one hand on designing and producing food products with bioactive ingredients—the so-called “functional foods” and “super foods”—for which health claims are made and on the other hand on finding suitable natural compounds that can replace the synthetic food additives (preservatives, antioxidants, colorants, aromas) [65]. Although a lot of investigations studied the antioxidant potentials of plant-derived wastes and by-products, the studies regarding their incorporation in food products are in early stages. Some examples of applications of recovered antioxidant compounds in foods are presented in the next paragraphs.

Carotenoids are a group of natural pigments beneficial for the health of humans due to their antioxidant properties but they are also used as food colorants. Most utilized in the food industry, for their antioxidant and coloring effect, are lycopene and β-carotene. These compounds, together with phytoene, phytofluene, lutein, ξ-carotene, γ-carotene and neurosporene, are found in tomato peel in considerable quantities. Besides the fact that the tomato peels contain up to five times more lycopene than the pulp, some studies also showed that the bioavailability of lycopene from processed tomato (submitted to heating and trituration) is greater than that from raw tomatoes [65–67]. Other fruit wastes (peels and seeds), sources of carotenoids, are avocado peel, banana peel, and mango peel. Carotenoids may be incorporated in different food products due to their antioxidant properties (improving the product shelf life), and colorant properties but also as nutritional constituents acting as precursor of vitamin A. Thus, some examples of products in which recovered carotenoids from wastes were incorporated include macaroni (nutritional, improving sensorial attributes before and after processing) [68], refined vegetable oils (antioxidant, increasing thermal stability) [69], and antioxidant edible films (improving shelf life) [9].

Another big class of natural pigments is represented by the polyphenols. They have a high capacity of scavenging reactive oxygen species (e.g., free radicals), thus being suitable to be used in food products as antioxidants. There are many fruits and vegetable wastes from which polyphenols can be recovered (see Table 1). A recent study evaluated the use of a polyphenol-rich extract from olive oil waste to act as a natural antioxidant in lamb meat patties [70]. The results were promising, showing that the polyphenolic extract could improve the product shelf life by preventing the discoloration and oxidative processes. Adding antioxidants from
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Potato peel extracts at concentrations ranging from 2.4 to 4.8 g/kg in minced horse mackerel had also positive impact on the product preservation. In the mackerel treated with polyphenolic extracts, the oxidation of proteins and lipids was prevented, considerably reducing peroxide value, tocopherol degradation, and generation of volatile secondary oxidation substances [71]. Similar results were obtained when polyphenolic extract from carob seeds peel was used as antioxidant in minced horse mackerel [72]. The polyphenolic extracts from potato peels were proved to have similar antioxidant capacity as the synthetic ones (butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT)) when incorporated in sunflower and soybean. The inhibition of thermal degradation of the oils may be attributed to the main polyphenolic compounds identified in potato peel extract: chlorogenic and gallic acids [73]. Brewers' spent grain—a by-product from brewing process—is a potentially valuable source of natural antioxidant compounds derived from the barley husk [74]. Ferulic acid, p-coumaric acids, and caffeic acid are in the highest concentrations, and they have been found with an excellent antioxidant potential, anti-inflammatory, and anticancer activities [75]. Brewers' spent grain flour or extracts can be added in bakery products, like enhancing their nutritional value [76]. Grape pomace, the winery waste, is particularly rich in polyphenols. The polyphenolic extract from muscadine grape pomace was tested in vitro to evaluate its capability to reduce the acrylamide formation. Acrylamide, a human carcinogen is a by-product of Maillard reaction, formed during the thermal treatment in different starchy food products (e.g., bread, potato chips). The results showed that the grape polyphenols (especially fractions recovered from skin and seed) significantly reduced the acrylamide level (by 60.3%) in potato chip model, even though there was no significant correlation between polyphenol antioxidant capacity and their potential for acrylamide inhibition [77].

Grape pomace is also an important source of fibers. Dietary fibers are generally known as being a health-promoting component of a diet. The consumption of this kind of fibers is connected with prevention, amelioration, and reductions in risks associated with cardiovascular disease, cancer, and diabetes [78]. Additionally, in the grape pomace, besides the dietary fiber, flavonoids are also present. The investigation of the antioxidant activity of flavonoids extracted from grape pomace has led to the elaboration of a new idea of antioxidant dietary fiber [79]. The presence of antioxidant compounds in the dietary fibers enhances their health benefits and their applications in pharmacological, cosmetic and food industries [80, 81]. Thus, for example, incorporating antioxidant dietary fibers into meat products could improve both their nutritional value and stability to oxidation. Grape pomace-added beef sausages (1% w/w) had a decreased rate of lipid oxidation and better sensorial attribute (taste and color) [82], while yogurt and salad dressings fortified with grape pomace likewise showed increased lipid oxidation stability without negatively influencing the consumers’ acceptance of the products [83]. Another source of antioxidant dietary fiber is the apple pomace. Obtained as a by-product after fruit processing, it is composed mainly of skin and pulp tissues which consist of pectin, cellulose, hemicellulose, lignin, gums, and phenolic compounds [32]. Among phenolic compounds found in apple pomace, phlorizin is used as a basic structure for a new class of oral antidiabetic drugs [84]. Other health benefits of apple polyphenols are antioxidant, antihypertensive, anticancer, antidiabetic, and hypolipidemic activities, thus making them appropriate to be used as nutraceutical [29, 85]. Many dietary polyphenolic components derived from
Plants have more efficient antioxidant activity in vitro than vitamins E or C and thus have the ability to lead significantly to the protective results in vivo. Several studies consider that fruit and vegetable dietary fiber could have better nutritional properties due to the synergistic effect of associated bioactive compounds such as flavonoids and carotenoids [86, 87].

Some of the antioxidant compounds recovered from vegetable wastes are already valorized in food products that can be found on the market. Thus, for example, some of the patented applications of recovered antioxidants include: the “sugar syrup” extracted with solvent from citrus peels which is used as food natural sweetener (AU1983/0011308D); lycopene from tomato waste used as food antioxidant and supplement (PCT/EP2007/061923); proanthocyanidines from grape and cranberry seeds used as coloring additive in soy sauce (JP1998/0075070); polyphenols from grape pomace or seeds used in food supplements (WO/1999/030724); ellagic acid (40%) and punicalagin (40%) from pomegranate rind and seedcase residues used as food antioxidants (CN2010/1531940); hydroxytyrosol from olive leaves extract as natural antioxidant in food stuff (EP 1582512 A1); and bioactive silverskin extract from coffee silverskin with potential applications in cosmetic, nutrition and health (WO2013/004873) [88].

5. Re-evaluation of food wastes as a source of valuable molecules

The interest of the research community in finding new or nonconventional sources of antioxidants is triggered by the numerous scientific evidences regarding the health effects of the dietary intake of antioxidants. Thus, by fortifying food products with antioxidant compounds, a supplementation of the daily diet with bioactive compounds may be achieved, therefore helping the human body to fight against damaging factors.

The key point for the recovery of natural compounds from fruits and vegetable wastes is to develop flexible strategies for each stage in which wastes are produced. Implementation of a modern technology by using green solvents and safer materials is strongly recommended. Obtaining purified active compounds is rather demanding for food industry and consumers, although this procedure involves an accurate safety assessment and long and sophisticated tests. From the laboratory scale and testing, the procedures used for the recovery of bioactive compounds are now facing the challenges for the scaled-up and further commercialization. The industrial recovery of antioxidants from food wastes, on one hand, is sustained by the numerous studies which have demonstrated their health benefits and, on the other hand, by the food companies which have foreseen the manifold applications of these bioactive compounds. Even though the scaled-up recovery processes may encounter some limitations (e.g., the variability in the composition of vegetable waste, waste collection and preservation method, purity of the isolated antioxidants, functionality of recovered antioxidants), with a proper management, a company could economically benefit by exploiting the recovered compounds to develop new functional food that meet the consumers not only organoleptic criteria but also their demand for healthier food products and at the same time addressing their concern for the environment [2, 6, 46, 48, 88].
Taking into consideration the health and food issues in the actual economical and environmental context, food wastes should no longer be regarded as a waste to be disposed but as a renewable source of valuable molecules that should be fully exploited. Still nowadays, despite their potential, food wastes remain often underexploited. So instead of the classical “waste to waste” perspective, new “waste to health” or “waste to food” perspectives should be considered especially because functional foods or nutraceuticals can be obtained by utilizing low-cost sources of bioactive compounds, ranging from antioxidants to dietary fibers, proteins, dietary lipids, natural colorants, or aroma compounds (e.g., essential oils). Health benefits of bioactive compounds from wastes will open up new research directions not only in functional food innovation but also in the medicine, pharmacy, or chemistry research fields.

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Author details

Sonia Ancuța Socaci1*, Dumitrița Olivia Rugină2, Zorița Maria Diaconeasa1, Oana Lelia Pop1, Anca Corina Fărcaș1, Adriana Păucean1, Maria Tofănă1 and Adela Pintea2

*Address all correspondence to: sonia.socaci@usamvcluj.ro

1 Faculty of Food Science and Technology, University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Romania

2 Faculty of Veterinary Medicine, University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Romania

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