



The Disposition of Bioactive Compounds from Fruit Waste, Their Extraction, and Analysis Using Novel Technologies: A Review

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Abstract: Fruit waste contains several bioactive components such as polyphenols, polysaccharides, and numerous other phytochemicals, including pigments. Furthermore, new financial opportunities are created by using fruit 'leftovers' as a basis for bioactivities that may serve as new foods or food ingredients, strengthening the circular economy's properties. From a technical standpoint, organic phenolic substances have become more appealing to industry, in addition to their application as nutritional supplements or functional meals. Several extraction methods for recovering phenolic compounds from fruit waste have already been published, most of which involve using different organic solvents. However, there is a growing demand for eco-friendly and sustainable techniques that result in phenolic-rich extracts with little ecological impact. Utilizing these new and advanced green extraction techniques will reduce the global crisis caused by fruit waste management. Using modern techniques, fruit residue is degraded to sub-zero scales, yielding bio-based commodities such as bioactive elements. This review highlights the most favorable and creative methods of separating bioactive materials from fruit residue. Extraction techniques based on environmentally friendly technologies such as bioreactors, enzyme-assisted extraction, ultrasound-assisted extraction, and their combination are specifically covered.

Keywords: fruit waste; bioactive substances; extraction technologies; sustainable

1. Introduction

The expansion of the global population, in addition to the shortages of food supply, necessitates a rise in food commodities, resulting in agricultural and food waste [1]. Food



Citation: Ali, A.; Riaz, S.; Sameen, A.; Naumovski, N.; Iqbal, M.W.; Rehman, A.; Mehany, T.; Zeng, X.-A.; Manzoor, M.F. The Disposition of Bioactive Compounds from Fruit Waste, Their Extraction, and Analysis Using Novel Technologies: A Review. *Processes* 2022, 10, 2014. https://doi.org/ 10.3390/pr10102014

Academic Editors: Carla Silva and Maria Angela A. Meireles

Received: 28 August 2022 Accepted: 27 September 2022 Published: 5 October 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). waste is any abandoned component of food, irrespective of its potential inclusion of substances with significant importance to food production or consumption [2]. Waste and food residues can be formed at any point along the food chain: owing to pests, disease, climate interference, and shipment. Furthermore, irregular-sized, physically unappealing, and damaged fruit may be discarded in several production procedures (washing, peeling, slicing) and in retail due to consumer damage and oversupply [3]. Despite this, food waste has a diverse and under-utilized chemical makeup of several different bioactive substances that may be utilized for applications in nutraceutical and pharmaceutical development, biomaterials, biorefineries, and the cosmetic and fragrance industries [4,5].

The increased levels of food waste are becoming one of the leading global food production problems by jeopardizing the food system's sustainability and increasing the pressure on the already fragile global food production system. [6]. Nearly 1.3 billion tons of foodstuffs are annually abandoned globally, despite 28% of farmland being used. It is equivalent to the global yield of 1.4 billion hectares of farmland, resulting in about one-third of the yearly world food output loss [7]. Based on these estimates, urban wastage is projected to reach 138 million tons by 2025 [8], posing a significant loss of other assets such as water, usable area, energy, and labor [9].

Food waste is a growing environment for several microorganisms [10] that may be utilized in food and beverage production [11,12]. Beneficial microbes produce enzymes that degrade organic matter and mitigate the effects of harmful pathogens [13]. It is well established that food waste is a valuable source of recovering highly valuable bioactives that are excellent sources of pigments, phenolic compounds, dietary fibers, sugar derivatives, organic acids, and minerals (Figure 1). The waste valorization idea is inextricably linked to sustainable recycling technologies with the main aim of increasing an item's value by transforming the unusable 'ignored' product into additional usable and functional resources. The resultant goods may include new compounds, commodities, fuels, and energy, as well as a variety of other items beneficial to local and global economies.

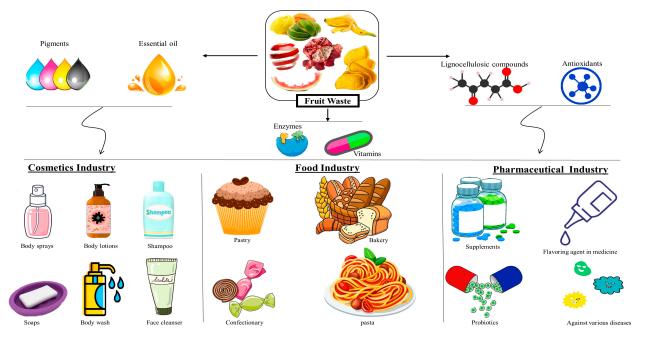


Figure 1. Graphical representation of fruit waste and its usage in different industrial sectors.

Therefore, this review aims to provide insights into biotechnological techniques used to extract fruit waste's bioactive and various phytochemicals.

2. Fruit Losses and Waste

Fruit production as an agri-business is expected to contribute to a substantial share of waste generation, with around 45% of the production waste in the supply and usage pathways, leading to a substantial volume of waste stuff [14,15]. The handling and transporting losses are approximately 25–30% [16]. Additionally, the waste generated from fruit juice manufacturing accounts for around 5.5 megatons (Mt) [17]. Every year, manufacturers generate up to 5–9 Mt of organic residue from grapes and other fruits, with around 20–30% of the waste being processed [18]. Other industrial food sectors, including canning and freezing, produce almost 6 Mt of waste material yearly, which accounts for 20–30% of leaves, stems, and stalks [18,19]. (Table 1).

Fruits	Type of Waste	Percentage of Losses (%)	References
Mango	Seed, peel	25.51	[20]
Apple	Seeds, peel	28	[21]
Banana	Peel	26.5	[22]
Guava	Peel, seeds	20–40 (developing countries) 10–15 (developed countries)	[23]
Papaya	Peel, seeds	57	[24]
Pineapple	Peel	32.12	[25]
Grapes	Stem, seeds, skin	53	[26]
Orange	Peel, seeds	29	[27]
Berries	Seeds, skin	20	[28]
Peach	Seed, peel	18–31	[29]
Apricot	Skin, seed	60–65	[30]

Table 1. Summary of different fruit losses and waste accumulation.

3. Bioactive Compounds in Fruit Waste

Fruit waste provides an enormous opportunity for the nutraceutical industry to utilize it as a source of 'naturally' derived nutraceuticals [31–33]. Plants are a significant reservoir of bioactive phytonutrients that can potentially be active in the management of several health conditions in addition to serving as a platform for developing new mainstream medications [34]. Several plant bioactives have exhibited strong antioxidant properties via different mechanisms of action, reducing the action of reactive oxygen species (ROS) and reactive nitrogen species (RNS) [35]. Consequently, these compounds can also reduce the negative impact of oxidative stress produced by the oxidation of lipids, proteins, DNA, and other biomolecules [36]. Since relatively recently, bioactive compounds are becoming increasingly popular for lowering the risk of developing chronic diseases such as cardiovascular disease, hypercholesterolemia, Parkinson's and Alzheimer's disease, several cancers [37], and type 2 diabetes, mainly due to the lower costs associated with mainstream medications [36,38].

4. Dietary Fiber in Fruit Waste

Dietary fiber primarily consists of carbohydrate polymers such as lignin, pectin, cellulose, and hemicellulose, which provide strength and stiffness to the plant cell walls. Dietary fiber is divided into two broad groups: soluble dietary fiber (SDF); gums (legumes, beans), pectin (legumes, grains), and mucilage (prickly pear cladode), and insoluble dietary fiber (IDF); lignin (vegetable aromatic alcohols vegetables), hemicellulose (wheat bran and grains), and cellulose (root vegetables) [39–41]. Different procedures, dry or wet treatment, microbiological approaches, and enzymatic methods, among others, are used to extract dietary fiber [42]. Since relatively recently, green extraction techniques, including steam, ethanol, and water extractions, coupled with ultrasonic-assisted techniques, high hydrostatic pressure, and pulsed field, have become more popular [43,44]. Applying

these safe and more environmentally friendlier extraction methods promotes high-quality separation that is repeatable and 'simple' to use while having a smaller ecological burden, even in laboratories with relatively limited equipment [45].

Fruit pomace is often treated as waste, being a residual item during treatment activities. These leftovers may also be an excellent source of dietary fiber. Appropriate handling of fruit waste at the commercial level is critical to reducing the large quantities amassed in landfills [46]. For example, apple pomace contains 15% and 36% soluble and insoluble fiber, respectively [47], and has been reported as a possible culinary component. The water-keeping capabilities of hemicellulose, pectin, cellulose, and lignin-containing items are reported to be between 9-10 g. Bread and other baked goods, milk commodities, medications, and pet supplies are prospective opportunities for these fiber-containing items [48]. Berry peel, stalks, and seeds include types of dietary fiber such as cellulose, lignin, pectin, inulin, and hemicellulose [40]. Grapefruit peels contain hemicellulose and cellulose, as well as trace quantities of pectin chemicals, and might act as a dietary fiber provider [49]. Around 51% (dry weight; d.w.) of all dietary fiber is provided by mango peels and fibrous pulp [40]. During the orange juice separation process, the pulp and peels of orange remains have nearly 35–37% (d.w.) dietary fiber, which is rich in hemicelluloses and cellulose (17-18% d.w.), lignin, and tannin (2-3% d.w.), as well as pectic components (up to 17% d.w.) [40]. The amount of dietary fiber obtained from pulp and peels using the peach juice separation method ranged from 31 to 36% (d.w.), with the majority being insoluble dietary fiber (20–24% d.w.). The soluble fiber proportion was 9–12% (d.w.), bigger than the soluble dietary fraction in grains and cereals [40]. Kiwi and pear pomace had 26 and 44% (d.w.) of total dietary fiber, respectively. Apple pomace had both more soluble fiber and methoxyl pectin [50]. The fiber fractions of pear pomace contained 34% lignin, 39% cellulose, 13% pectin, and 19% hemicelluloses [40,51]. The total dietary fiber percentages in different fruit wastes are presented in Table 2.

 Table 2. Percentage of dietary fiber content in different fruits (d.w.).

 Total Dietary Fiber
 Incoluble Dietary Fiber

Fruits	Waste	Total Dietary Fiber Percentage (%)	Insoluble Dietary Fiber Percentage (%)	Soluble Dietary Fiber Percentage (%)	Reference
Mango	Seed, peel	51.2	32	19	[52,53]
Apple	Seeds, peel	61.9	36.5	14.6	[54]
Banana	Peel	44.03	0.73	0.13	[55,56]
Guava	Peel, seeds	48.55-49.42	95 of total dietary fiber	4.00-4.52	[57]
Papaya	Peel, seeds	44.66	-	36.99	[58]
Pineapple	Peel	46-48	44–47	0.78-0.80	[59]
Grapes	Stem, seeds, peel	25.8	17.4	8.4	[60]
Orange	Peel, seeds	0.58	0.53	0.05	[61]
Peach	Seed, peel	36	20-24	11–12	[62]
Apricot	Skin, seed	4.01	n.a.	1.07	[63]
Watermelon	Peel, seed	17.28	n.a.	n.a.	[64]

Note: n.a.—results are not available.

5. Phenolic Compounds

Some of the most important natural antioxidants are phenolic compounds [65–67]. Polyphenols have grown in popularity as phytochemical substances due to several potentially beneficial health properties related to cardiometabolic illnesses and oxidative stress [11,35,68,69]. Some phenolic compounds (tannin, flavonol, flavan, and neolignan) have also exhibited antibacterial properties against viruses, bacteria, and fungi [70].

Grape peel and pomace are abundant in resveratrol (3,5,4'-trihydroxystilbene), which is left unused and created in large quantities as a byproduct of wine production. Resveratrol was reported to enhance NF- β cell anti-inflammatory reaction, free radical scavenging action, and activity of the cytochrome P-450 enzyme, which promotes liver detoxification. It also reduces cellular damage and mitochondrial dysfunction [71,72].

Date palm fruit (*Phoenix dactylifera*) is a significant source of flavonol glycoside and β -glucans. These compounds were reported to prevent oxidative cell injury and reduce damage caused by conventional chemotherapy mainly via their antioxidant activity [73,74].

Olive oil contains large waste production high in secoiridoids, hydroxytyrosol, and lignans [75]. These compounds high in biowaste have exhibited antiplatelet and antiinflammatory properties [76,77]. Furthermore, palm and soybean oil waste has been identified as a valuable source of potassium, carbohydrates, sodium, iron, magnesium, calcium, trace vitamins, minerals, isoflavones, soyasaponins, and polyphenols [78]. These compounds have been associated with improvements in several health outcomes.

The manufacturing of pomegranate juice generates many leftovers and contains a high concentration of punicalin, punicalagin, and ellagitannins which have a high antioxidant activity [79]. Similarly, apple peel is a good source of polyphenols, reportedly having anticancer, antibacterial, and cardioprotective properties [80]. The types of polyphenols and their structures in the waste of different fruits are reported in Table 3.

Fruits	Waste	Phenolic Compounds	Structure				Reference
Mango	Seeds, peel	1: Ellagic acid 2: Quercetin 3: Galic acid 4: Mangiferin	H H Ellagic acid	, , , , , , , , , , , , , , , , , , ,	Gallic acid	Mangiferin	[81]
Apple	Seeds, peel	1: Quercetin 2: Epicatechin 3: Phloridzin 4: Phloretin 5: Procyanidin B2	Epicatechin	Phloridzin	Phloretin	Procyanidin B2	[82]
Banana	Peel	1: Hydroxycinnamic acids (HCA) 2: Flavonols 3: Flavan-3-ols 4: Catecholamines	HCA	Flavonols	Flavan-3-ols	H,C HO H,C HO H,C HO H Catecholamines	[83]
Guava	Peel, seeds	1: Galic acid 2: Galangin 3: Catechin 4: Homogentistic acid (HA) 5: Caffeic acid	Galangin	HO Catechin	он Сн НА	HO Caffeic acid	[84]

Table 3. Phenolic compounds and their structures identified in fruit waste.

Fruits

Papaya

Pineapple

Grapes

Orange

Peel, seeds

Anthocyanins

Naringin

		Å	A A		ОП
		Salicylic acid	Gentisyl alcohol	Chrysin	PA
Peel, stem, crown	1: p-Coumaric acid (p-CA) 2: Catechin 3: Epicatechin 4: Cinnamic acid 5: Vanillin 6: Syringic acid	ностори	Linnamic acid	Vanillin	
		p-CA	Chillannic actu	Valiiiiii	Syringic acid
Stem, seeds, peel	1: Hydroxybenzoic acid 2: hydroxycinnamic acids (HCA) 3: Anthocyanins 4: Proanthocyanidins 5: Catechins	H H H			J. J

Hydroxybenzoic

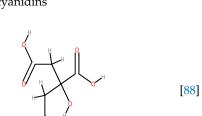
Ferulic acid

6: Flavonols

1: Quercetin
 2: Gallic acid:
 3: Ferulic acid

4: Naringin 4: Hesperitin 5: Citric acid Proanthocyanidins

Hesperitin



Citric acid

Reference

[85]

[86]

[87]

Table 3.	Cont.
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Fruits	Waste	Phenolic Compounds	Structure			Reference
Peach	Seeds, peel	1: Chlorogenic acid 2: Neochlorogenic acid 3: p-Coumaric acid 4: Gallic acid 5: Flavonols 6: Flavan-3-ols 7: Anthocyanidins	Chloroge	enic acid	$ \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & \\ & \\ & \\ $	[89]
Apricot	Skin, seeds	1: Gallic acid 2: Chlorogenic acid 3: Caffeic acid 4: Quercetin-3-galactoside (Q-3-galactoside) 5: Quercetin-3-glucoside (Q-3-glucoside) 6: Quercetin-3-rutinoside (Q-3-rutinoside) 7: Kaempferol-3-rutinoside (K-3-rutinoside)				[90]
Watermelon	Peel, seeds	1: Gallic acid 2: Synapic acid 3: Myricetin 4: p-anisic acid	Q-3-galactoside $H_{3}C \xrightarrow{O} + + + + + + + + + + + + + + + + + + +$	Q-3-glucoside	K-3-rutinoside	[91]
			Sinapic acid	Myricetin	p-anisic acid	

Fruits	Waste	Phenolic Compounds	Struc	ture	Reference
Kiwi	Peel	1: Benzoic acid 2: Chlorogenic acid 3: Gallic acid 4: Vanillic acid 5: Delphinidin 6: Cyanidin			[92]
Berries	Peel, seeds	1: Caffeic acid 2: Quercetin 3: Proanthocyanidins 4: Gallic acid 5: Secoisolariciresinol	Benzoic acid $\downarrow \downarrow $	Delphinidin	[93]

6. Fruit Waste as a Source of Flavoring Agent

Due to the rising consumer desire for organic, conventional, and healthy resources, the industrial requirements for scents, perfumes, and tastes have grown significantly over the past few decades. Plant by-products can extract various flavoring substances, and fruit waste can be a significant raw material supplier. Solid state fermentation (SSF) is a conversion process that has separated several possible products from fruit waste, including enzymes, ethanol, flavors, lactic and citric acid, methane, and different food components [94]. Vanillic acid is used to make vanillin (4-hydroxy-3-methoxy benzaldehyde), which is extensively used in the culinary, cosmetic, detergent, and pharmaceutical industries [95]. Ferulic acid, a precursor to vanillic acid, is present in pineapple peel remnants. The hydrolytic cleavage of citrus fruits commonly generates rhamnose, which is also a source of the strawberry flavoring "furaneol" (2,5-dimethyl-4-hydroxy-3(2H)furanone) [96]. After extracting volatile chemicals from pineapple processing waste, over 35 volatile molecules were identified, including ketones (9%), aldehydes (9%), alcohols (29%), esters (37%), and acids, which were the most often recognized chemicals (6%) [97]. This feature suggests that fruit production waste may produce fragrant natural essences; after re-introducing them into the main product, it could improve the sensory quality of items such as pineapple juice concentrate [98]. An overview of flavors, enzymes, aromas, and organic acids found in fruit waste is provided in Table 4.

7. Important Enzymes in Fruit Waste

Enzymes are biological catalysts for various purposes, from brewing to paper, pulp, bread, and detergent production [99]. These are often chosen over synthetic catalysis owing to their high substrate sensitivity and stringent but reliable operating parameters. All biological processes contain enzymes, and nowadays, large quantities of any bacterium's enzymes can be produced to suit the demands of various industries, thanks to the proliferation of recombinant DNA technology [100]. Pre-treatments are frequently employed in lignocellulose-based primary material processing techniques in which mechanical, biochemical, or a combination disrupt the intricate plant structure and boost digestibility [101,102]. Different processes employing various agro-industrial residues can produce enzymes such as cellulase, α -amylase, pectinase, and protease, among others.

7.1. Amylases

This category consists of three enzymes: glucoamylase, α -amylase, and β -amylase. The methodologies of SSF and SMF have been widely applied for amylase synthesis, although SMF has typically been the preferred method for producing economically suitable amylases since numerous environmental parameters (pH and temperature) can be readily regulated and managed [103]. Numerous fruit leftovers are employed as a substrate for amylase syntheses, such as potato peels [104], loquat kernels [105], citrus waste [106], cassava waste [107], date waste [108], and mango kernels [86]. Furthermore, using *Aspergillus niger*, α -amylase can be manufactured from orange residue powder [109]. Several bacterial species, including *Aspergillus oryzae*, *Aspergillus tamarii*, *Aspergillus awamori*, *Rhizopus oryzae*, *Bacillus subtilis*, *Bacillus licheniformis*, *A. niger*, *Thermomyces lanuginosus*, and *Candida guilliermondii*, are commonly used to produce different amylases. The most often used varieties in commercial production include *B. subtilis*, *A. niger*, and *R. oryzae* [108]. Amylases are frequently utilized in the processing industries for various goods such as moist cakes, chocolate cakes, starch syrup, fruit juices, and so on, as well as numerous procedures such as digestive aid production, baking, and brewing [94].

7.2. Cellulases

Cellulases include β -d-glucosidase, endo-1,4- β -d-glucanase, and exo-1,4- β glucanase. They serve food industries, notably recovering phenolic substances from grape peels and releasing aroma-rich chemicals [94]. Cellulases are commercially important enzymes owing to their critical involvement in bioethanol synthesis [110] and can be used in brewing, bread production, paper, pulp, textiles, and detergents manufacture [111]. Cellulase enzymes are produced by various bacterial and fungal species, including *Trichoderma reesei* boosted strains [112]. Some of the most commonly used fungal species to manufacture cellulases include *Melanocarpus* sp., *Penicillium* sp. *Schizophyllum commune, Aspergillus* sp., and *Fusarium* sp. [113]. The development of low-cost cellulase manufacturing techniques has been a key focus of research over the last two decades due to the impact on the economics of bioethanol production. When banana peel was employed with an inoculum size of 1.5 109 spore/flask and cultured at 30 °C for 14 days, *Trichoderma viride* GIM 3.0010 produced cellulase [114].

7.3. Pectinases

Pectinases are enzymes that break down pectic materials, which are essential constituents of the cell walls of fruits. Pectate and pectin lyases may break glycosidic connections to structure the lengthy carbonyl group, whereas pectin esterase works with methoxyl units. Pectinase is produced via SSF of grape pomace using *A. awamori* yeast [115]. Pectinases are used in the wine and fruit juice industries to reduce turbidity in the final product and can help with stability and filtering by enhancing the coloring of the fruit extract [116]. Various agricultural residual variations have been explored and evaluated for pectinase synthesis employing various bacteria. Grape and apple pomace were thoroughly studied to assess their suitability as pectinase manufacturing substrates [117]. Pectinases have also been created from a waste combination. Sugar cane bagasse and citrus peel are fermented in solid-state mode to create pectinases while preventing overheating issues [118]. Citrus waste and sugarcane bagasse were used in the solid-state fermentation of pectinases in a pilot-scale packed bed bioreactor [119].

7.4. Invertase

A glycoprotein called invertase, often referred to as β -fructofuranosidase, catalyzes the hydrolysis of sucrose into glucose (dextrose) and fructose. Invertase activity is maximal at a temperature of 55 °C and a pH of 4.5. *Saccharomyces cerevisiae* is the most common microorganism employed in the industrial manufacture of invertase enzymes [119]. Invert sugar is made using invertase, and the latter has a lower crystallinity value than sucrose. Hence, it keeps the item soft and fresher for a longer time [120]. Sucrose is completely inverted when invertase is used without creating contaminants [121]. Invertase is especially utilized in manufacturing sweets, jam, confectionery, and medicinal items [122].

7.5. Other Enzymes

The most common enzymes created using SSF procedures include proteases, xylanases, tannases, and laccases [123]. These enzymes are also widely employed in the food industry to generate key products; tannase is used to clear fruit liquids and beer and to make colors, gallic acid, and instant tea [124]. Palm kernel cake and tamarind seed powder are utilized by *A. niger* to produce tannase. For palm kernel cake and tamarind seed powder, the tannase production was 13.03 and 6.44 per gram (d.w.), respectively [94]. Xylanase extracts plant oils from starch that can provide textural variations and food thickeners for baked foods [125]. Tomato pomace can be combined with *Coriolus Versicolor* as the carbon source for laccase synthesis, and it had the highest laccase titer (362 U/L fermentation broth) [94]. *Trametes trogii* (*Berk.*) and *Trametes Versicolor* have also removed the laccase enzyme from apricot seeds and shells [126]. Proteases continue to be the dominant enzymes because of their vast application in the washing and dairy sectors. Various agroindustrial wastes, as well as fruit wastes, have been extensively researched for protease synthesis [127].

Since their introduction as the consumer's preferred sweeteners in the food and pharmaceutical sectors, fructose and fructooligosaccharides, as opposed to sucrose, have increased the importance of inulinase. Inulinase is an enzyme that operates on inulin; it has a glucose molecule at the end of a polyfructose (fructan) chain. The fructose units in inulin are joined by a β -2,1-linkage [128]. Exo-inulinases and endo-inulinases are two

types of inulinases [129]. Aspergillus niger, Penicillium sp., Actinomyces viscosus, Streptococcus salivarius, Chrysosporium Pandorum, and Kluyveromyces fragilis have all been shown to synthesize inulinase [119]. When cultivated bagasse, wheat bran, banana peel, rice bran, orange peel, and a recently recovered Saccharomyces sp. using spontaneously fermented sugar cane synthesized inulinase [130].

8. Organic Acids

Essential organic acids for the culinary and pharmaceutical industries are citric and lactic acids. Fermentation with different molds, yeasts, and bacteria can create citric acid. However, *A. niger* remains a popular mold species commercially synthesizing citric acid [131]. The SSF procedure was utilized to manufacture citric acid from cassava bagasse and coffee husk employing *A. niger*. Cassava bagasse is a good substrate for producing high citric acid levels [132]. *A. niger* has also used apple trash as a substrate source in the manufacture of up to 80% citric acid [133] and mandarin, pineapple, and mixed fruit waste, which provided 50%, 51.4%, and 46.5% citric acid, respectively [134]. Lactic acid is an essential member of the carboxylic acid family because it has ramifications in the food and non-food sectors. It is generally used as an acidulant and preservative [135]. The expense of raw materials is the key issue in synthesizing lactic acid. Lactic acid may be created by a variety of bacteria utilizing fruit byproducts. *Lactobacillus plantarum, Lactobacillus casei,* and *Lactobacillus delbrueckii,* have been employed to manufacture lactic acid from substrates such as green peas, sweet corn, orange, potato peel, cassava, and mango residue [136].

Fruit Waste	Value-Added Products Enzymes	Microorganisms Used	Organic Acid	Flavor	References
Banana	Amylases Cellulases Laccases, xylanases Lipases	Bacillus megaterium, pseudomonas fluorescence, penicillium putida, cellulomonas carte, Bacillus subtilis, Bacillus sp., Aspergillus niger, Aspergillus spp. MPS-002, Phylostica spp. MPS-001, Trametes pubescens, Bacillus sp., Aspergillus niger, Penicillium Citrinum, Aspergillus foetidus	Glutamic, aspartic, glutaric, quinic, glyceric, glycolic, and succinic acids plus several keto acids	Vanillin in banana peel is used as an aroma and flavoring agent in the food industry	[139–143]
Mango	Cellulases	Fusarium solani, Aspergillus niger		Decanal, 1-octen-3-one, nonanal, limonene, β-damascenone, and 2-nonenal	[141,143,144]
Apple	ethyl butyrate Laccases Pectinases Xylanases	Trametes hirsute, Lentinus edodes, Aspergillus foetidus, Trichoderma harzianum 1073 D3	Citric acid	Ethyl acetate	[141,143]
Orange/lemon	Invertases Lipases Pectinases α-Amylases	Aspergillus flavus, Trametes hirsute, Pleurotus sp., Chaloropsis thielarioides, Colletotrichum Gloesporioides, Bacillus sp., Aspergillus niger, Penicillium Citrinum, Aspergillus foetidus, Aspergillus niger		Citral, Limonene	[141,143]
Pineapple	Invertases Pectinases	Aspergillus flavus, Penicillium chrysogenum, Aspergillus foetidus, Trichoderma koeningi	Citric acid, Acetic acid	Some aroma compounds were found in the volatiles of pineapple fruit. These compounds include esters, aldehydes, alcohols, acids, lactones	[141,143,145]

Table 4. Enzymes, organic acids, and flavor in different fruit waste products.

Fruit Waste	Value-Added Products Enzymes	Microorganisms Used	Organic Acid	Flavor	References
Pomegranate	Invertases	Aspergillus flavus	Primarily citric and malic acids	Glucose and fructose	[141,143,146]
Kiwifruit	Laccases	Trametes hirsute	Quinic acid, citric acid, malic acid and tartaric acid	(E)-2-hexenal and hexanal	[141,143,147,148]
Grapes	Laccases Pectinases Cellulases Xylanases	Trametes hirsute, Aspergillus foetidus, Aspergillus awamori	Tartaric and malic acids	Volatile thiols	[141,143,149]
Watermelon	Xylanases	Trichoderma harzianum 1073 D3, Trichoderma sp.	malic acid, citric acid, and oxalic acid	_	[143]
Papaya	—	—	Acetic acid	—	[143]

Table 4. Cont.

9. Bioactive Compounds Extraction

Bioactive chemicals provide a valuable source for developing nutritional supplements, food additives, and functional foods [150]. Based on relatively recent findings, agricultural residues might be an excellent reservoir of useful bioactive substances. Most of these bioactive chemicals have been shown to have potentially health-promoting effects such as anti-tumor, cardioprotective, antiviral, antibacterial, and anti-obesity, among others. High food waste is produced from pulp post-processing (to make juice, jams, and purees) [40]. Extraction procedures may differ depending on the bioactive substances being extracted. Several parameters, including heat, plant components, pressure, and solvent type, can all impact the separation processes [151]. Fruit waste functional compounds may be collected in many ways, classified as 'old' and 'innovative' processes, and are presented in Figure 2.

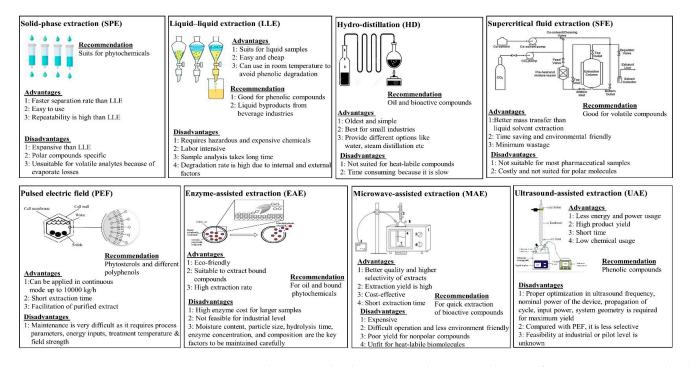


Figure 2. Some advantages, disadvantages, and recommendations of various extraction methods. References of each mentioned extraction method are as follows: SPE [152], LLE [153], HD [154], SFE [155], PEF [156], EAE [157], MAE [158], UAE [154,156].

9.1. Conventional Extraction Techniques

As they have been employed for a lengthy time, classical procedures are termed customary approaches. These processes are built on the solvent extraction capacity and the delivered energy, or their combination. Hydro-distillation, Soxhlet extraction, and maceration were identified as 'traditional' extraction procedures [159].

Soxhlet extraction has long been used as a traditional method for extracting important bioactive components from diverse plant parts; however, it was created exclusively for lipid extraction [160]. New methodologies are linked to this traditional extraction technology since it serves as the main model for new advancements. A very small quantity of dry material is placed in a thimble and a distillation beaker filled with the preferred solvent. If the solution reaches an overflow point, it is aspirated from the thimble holder and transferred to the distillation flask by a siphon. The extract is held in this combination, which transfers it into the liquid in bulk. The extract solute stays in the distillation flask, whereas the solvent stays with the solid plant. The solvent is repeatedly added to the solid plant material while the extracted solute remains in the distillation flask. The procedure is continuously repeated until the extraction is complete [94].

Hydro-distillation is an approved method used as a reference for extracting essential oil [161]. The proposed program was used to evaluate operating variables (such as heat and fuel usage). To isolate oil by hydro-distillation, fragrant plant material is put into a still, and appropriate amounts of water are added and brought to a boil. Alternatively, the live steam is added to the botanical charge. Under the influence of heated vapor and liquid, the oil is released from the oil glands in the plant tissue. Condensation occurs when water and oil vapor are passively chilled. Condensate flows from the condenser into a separator, where oil and distillate water are mechanically separated [162].

Maceration is a generic procedure for extracting therapeutic herbs usually utilized for galenical medicines [163]. The basic concepts and methods in maceration, percolation, and infusion for crude drug extraction are the same as those in leaching, in which soluble elements from solid substances are extracted using a solvent. Leaching techniques might be as basic as physical solution or dissolving. Several variables influence extraction operations, including the pace of solvent transport into the mass, the speed of dissolution rate of the soluble elements by the solvent, and the rate of solution transport out of the insoluble material.

9.2. Novel Extraction Techniques

Different approaches can be used to extract bioactive substances found in agricultural waste. Various approaches allow for the utilization of the best approach for the retrieval of particular chemicals. Bioactive ingredient extraction approaches are mostly focused on enzyme-assisted extraction, solvent extraction (SE), solid-liquid extraction, pulsed electric field (PEF), microwave-assisted extraction (MAE), subcritical water extraction (SCW), ultrasound-assisted extraction (UAE), and supercritical fluid extraction (SFE).

9.2.1. Solid–Liquid Extraction (SLE)

It is among the most extensively used methods for extracting phenolic chemicals from agri-food residues [164]. However, it involves long processing times, high prices, limited outputs, and the employment of organic solvents, which, while great for phenolic substance solubility and extraction, have several inherent problems such as toxicity, temperatures, and non-biodegradability [165,166]. Contrarily, water appears to be the preferred solvent for polar and hydrophilic substances [167]. Green solvents are, therefore, greatly needed since they can perform excellent extraction while being less costly and having a less negative influence on the ecosystem than traditional organic solvents [167].

Deep eutectic solvent (DES) is a novel, eco-friendly, green solvent extraction procedure created and used to recover phenolic compounds [167,168]. A study by Abbott et al. [169] was the first to describe DES preparation, which utilizes a mixture of a hydrogen bond donor (HBD) and acceptor (HBA) at the proper temperature (HBD) [169]. DES has numerous

benefits over typical organic solvents, including low cost, ease of manufacture, and ease of availability. Furthermore, most are biodegradable and have relatively little toxicity [168]. The salt choline chloride (ChCl), inexpensive and non-toxic, is most frequently utilized in creating DES, while ethylene glycol, urea, and glycerol are the most often utilized HBDs.

Furthermore, carboxylic acids, amino acids, alcohols, and sugars are employed [170]. DES was created by combining primary metabolites with bio-renewable beginning ingredients. The 'natural deep eutectic solvents' were created by mixing substances from nature that are key players in the solubilization, storage, and movement of molecules in living cells and animals [171].

A relatively new solid–liquid extractor that reaches equilibrium between the outside and interior of a solid matrix suspended in a suitable solvent by producing a negative pressure gradient is called the Naviglio Extractor R. (Naviglio's Principle). It is feasible to deplete the solid matrix and extract bioactive compounds by employing additional extractive cycles [172]. This innovative solid–liquid dynamic technique has various benefits, including the ability to do extractions at room temperature and thermal stress reduction in thermolabile compounds [172]. Additionally, using high pressure enables a decrease in extraction time and an improvement in extraction accuracy.

9.2.2. Solvent Extraction Technique (SET)

Various organic solvents are applied to the appropriately sized raw material to pull out any complex soluble components and extra flavoring, including several coloring chemicals and anthocyanins [173]. Samples are often centrifuged and screened to eliminate solid residue before being employed as an addition, food supplement, or in the creation of functional foods [174]. Solvents are recyclable, non-volatile, biodegradable, non-toxic, and have a low energy cost [175]. Neoteric solvents are structurally new or unconventional structures with physical chemical characteristics that may be tailored for several uses via precise management of the chemical components [176]. Eutectic solvents, ionic liquids, and fluorous solvents have attracted the most consideration among neoteric solvents. Fluorescent solvents have been used to extract metals and chemical molecules [177]. One popular solvent is ethyl lactate [178]. Solvents extraction has been used to retrieve phenolic substances, sinapine, and flavonoids from seeds of sunflower, mustard Crambe, and rapeseed, as well as caffeic acids and rosmarinic from basil wastewater, ellagic acid, anthocyanins, polyphenols, and flavonoids from pomegranate peel, carotenoids, and phenols from tomato waste [179–184]. The extraction procedure depends on the choice of solvent. The most common solvents for extraction using traditional techniques at the industrial level are alcohols (ethanol and methanol). However, a variety of solvents are used, including non-chlorinated solvents such as acetone and acetonitrile, and chlorinated solvents such as chlorobenzene, chloroform, and carbon tetrachloride [185]. A solvent with a rapid mass transfer, low boiling point, and nontoxicity might be an excellent choice. The extraction's effectiveness is impacted by particle size. Smaller particles improve the solvents' ability to penetrate them, but if they are too small, the subsequent filtering procedure will be challenging [186].

Because of its cheap operational costs and simplicity of operation, the solvent extraction method is superior to other similar techniques. However, this approach employs hazardous solvents, necessitates an evaporation/concentration phase for retrieval, and typically necessitates huge volumes of solvent and a lengthy time frame. Furthermore, with the high heat of the solvents throughout the extended extraction durations, the likelihood of thermal destruction of natural bioactive constituents cannot be overlooked. Other technologies, such as ultrasonic, microwave extraction, Soxhlet, or SFE, have increased solvent extraction yields [187].

9.2.3. Enzyme-Assisted Extraction (EAE)

Enzymes are often used to recover bioactive substances from food waste. Pectin, hemicellulose, and cellulose, three polysaccharides found in plant cell walls, serve as barriers to releasing intracellular chemicals. Plant cell wall polysaccharides are broken down and depolymerized by enzymes such as pectinase, xylanase, β -gluconase, and β -glucosidase, enabling associated compounds to be released [188]. Enzyme-aided extraction is considered a more ecologically friendly way of extracting bioactive compounds and oil since it employs water as a solvent rather than organic solvents [157]. Using enzyme preparations alone or in combination can improve the extraction and destruction of plant cells to release bioactive substances. Traditional solvent-based extraction processes can be replaced by enzyme-assisted extraction. It is based on enzymes' ability to catalyze interactions in aqueous media under moderate process conditions [189].

9.2.4. Fermentation

Fermentation is probably among the earliest product-specific techniques for converting food waste products into usable goods via microbes [190]. The most common fermentation procedures are solid state and submerged liquid fermentation. Both procedures have been employed for research and industrial purposes; however, some achieved higher outputs than others due to different metabolism performed by microorganisms in both approaches [191].

The fermentation technique in which microorganisms grow on solid substrates without exposed liquid is known as *solid-state fermentation* (*SSF*) [192]. The main objective of SSF is to maximize nutrient absorption from the medium for processing by employing microorganisms such as fungus or bacteria. *SSF* is further characterized based on whether the seed culture utilized for fermentation is pure or mixed [193] and can be divided into two groups based on the solid phase. In the initial variant of SSF, the solid acts as both a support and a food supply. These solid substrates are produced by food companies such as the bean, sugar beet, potato, cassava, pulp, and grain industries, among others [194].

Submerged fermentation (SmF) is a form in which the medium is liquefied or fermented in a body of water. SmF is primarily employed in industrial operations because of its high output, low price, and little contamination. However, SmF has significant drawbacks, such as physical space and energy or water needs, among others [195]. Because of various advantages, the enzyme synthesis by SmF has been employed during the last century as opposed to SSF. Furthermore, this fermentation technique is more easily accessible to industry and research due to the simplicity of system management and sterilizing [196].

Numerous forms of solid substrates derived from agricultural waste have been employed for solid-state fermentation; each has a potentially higher dietary function in terms of being a source of vitamins, peptides, and fiber [193]. Because macro- and micro-molecules in diet have tremendous value in human and animal diets, solid-state fermentation is an excellent method for improving their digestibility and bioavailability [197]. Various types of research have investigated the influence of SSF on the physiological qualities of agro waste and revealed the superiority of solid-state fermented substrate over unfermented substrate [193].

9.2.5. Pulsed Electric Field (PEF)

Pulsed electric field (PEF) is a relatively new and innovative approach for obtaining useful molecules from fruit leftovers and residues. This unique separation process includes applying high-voltage microsecond pulses to a material 'sandwiched' between two electrodes [198–202]. A PEF generation unit, a suitable product process apparatus, a treatment container, and monitoring and surveillance equipment comprise a standard approach to pumpable fluid processing [203]. PEF improves the recovery rates and outputs of various chemicals while having no impact on the grade of the retrieved substances. The pulse amplitude in the PEF apparatus varies between 0.1–0.3 to 20–80 kV/cm. Mild electric fields (0.5 and 1 kV/cm; lasting 104–102 s) cause cell membrane breakdown with minimal warming pattern. As a result, PEF is an excellent separation method for heat-sensitive chemicals. The key process variables that characterize PEF treatment are the electric field strength and processing time. The processing characteristics are determined by the par-

ticular energy and the quantity of supplied pulses [204]. It is a non-thermal method that improves recovery when used as a pre-treatment over heat-based pre-treatment. Due to the specific extraction of intracellular molecules, the energy needed is modest and does not affect the general architecture of the cell. Because the extracts are greater, no supplementary purifying stages are required, resulting in decreased overall capital expenses [205]. The greatest polyphenol production was acquired at a field value of 7 kV/cm, while the highest naringin and hesperidin output was achieved at a field power of 5 kV/cm, with a treatment duration of 60 ms and a pressing duration of 30 min [206]. Temperatures of 35 °C and 50 °C yielded the maximum anthocyanin and polyphenol yields, respectively [207].

9.2.6. Microwave-Assisted Extraction (MAE)

Due to the ionic conductivity and dipolar rotation of inner molecules, heat is generated within the material during Microwave-Assisted Extraction (MAE). The temperature is required for cell wall rupture, which allows bioactive compounds to 'move away' from the cell wall and into the extraction system [208]. MAE has the benefit of requiring a shorter extraction period; hence, it has been used on various waste streams to recover a variety of bioactive substances. As a consequence of mass and heat gradients formed in the matrix, separate processes have been seen in MAE, including solvent penetration into the matrix, component solubility or dissolution, separation of the fluid and remaining solid phase, as well as the transfer of solubilized chemicals from the inert material to the solution phase [209]. MAE can be performed in sealed extraction vessels that run at extreme pressures and temperatures, enabling larger product yields, or in exposed vessels that function at lower atmospheric pressure. The latter technique is well suited to thermolabile chemicals and has the benefit of needing low-cost equipment capable of processing larger volumes. Recently, devices that work in a vacuum or nitrogen atmosphere have also been developed [209].

9.2.7. Ultrasound-Assisted Extraction (UAE)

Ultrasound-aided extraction (UAE), like MAE, decreases the time and amount of solvent required to remove phenolic compounds from agri-food residues proficiently. One of the relatively easiest extraction methods is UAE, which needs basic laboratory tools such as an ultrasonic bath [164,210–212]. The method is centered on the cavitation phenomenon, which is brought about by the contraction and extension phases that are brought about by ultrasonic waves with a frequency of 20 kHz to 100 MHz traveling through the substance. The cavitation bubbles explode, resulting in inter-particle interactions that, among other things, cause particle breakup and speed up the diffusion of substances that can be extracted into the solvent [164]. Specimen properties such as uniformity, rheology, and particle motility can thus have a considerable impact on ultrasonic energy dispersion and, as a result, the efficiency of the UAE. It is typically conducted in static circumstances, in a sealed jar without solvent replacement, or in a dynamic condition, where new solvent is periodically provided [209].

9.2.8. Supercritical Fluid Extraction (SFE)

Another sustainable technique built on supercritical CO_2 (sc CO_2) has also been projected to solve ecological difficulties associated with traditional approaches. Sc CO_2 has obvious advantages over standard solvent-based approaches. It permits the preferential isolation of molecules soluble in sc CO_2 , making it ideal for lipophilic chemicals such as lipids, as no concentration steps are required [213]. Introducing a co-solvent (such as ethanol, which is widely accepted by many manufacturing industries) can change the polarity of the sc CO_2 , enabling the separation of more polar compounds [214].

Furthermore, the operating heat can be adjusted sufficiently to prevent thermolabile compounds from degrading. Recent findings demonstrate a significant superiority over traditional extraction concerning collection, specificity, chemical durability, duration, and total power savings [215]. The dissolution of desired chemicals in scCO₂ is an important

factor in SFE that influences the separation rate. Heat is an important thermodynamic factor that primarily influences targeting chemical solubility. In particular, increasing the pressure increases supercritical fluid density and solvation power. The raw ingredients are put in an extraction vessel fitted with thermal controls to sustain the proper parameters during the extraction phase. After that, a pump fills the extraction vessel with liquid. The output is gathered by a tap installed in the separators' bottom part after the fluid and dissolved chemicals are transferred to the separators. The fluid is ultimately gathered, recycled, or discharged into the environment. This approach uses a wide range of chemicals as solvents, but the choice of supercritical fluid is essential for the proper functioning of the process [216].

9.2.9. Subcritical Water Extraction (SWE)

Subcritical water extraction (SWE) is a rapidly growing process for extracting phenolic chemicals from various foods. The treatment of food ingredients has proven to be one of supercritical fluids' most successful uses. It has been used to assess the concentrations of bioactive substances from foods, lignans, and other organic compounds found in lignans, berries, and other ecological biomasses [217]. Subcritical water has a temperature between 100 and 374 °C and high enough pressure to make it liquid (below the critical pressure of 22 MPa). Less time is spent extracting, less solvent is used, the extraction quality is greater, and SCW is more environmentally friendly than other traditional extraction methods [218,219]. Using SWE to process agricultural biomass at lower temperatures simultaneously catalyzes chemical processes such as the gradual breakdown of polysaccharides into xylooligomers, xylose-monomers, and other degradation products [220]. SWE is used to bleach the ground, recovering free fatty acids and oils. Utilizing SWE, lignans, carbohydrates, and proteins were recovered from flaxseed meal. Hydrothermal techniques produced mono- and oligosaccharides from agricultural and industrial leftovers [220,221].

The number of phenolic chemicals extracted from mango skins utilizing SCW extraction was more effective than Soxhlet extraction. As a result, SCW extraction provides a green option to the traditional approach of extracting phenolic chemicals from agricultural residues that use organic solvents [222]. Other uses include recovering oregano, potato peels, Thymbra spicata essential oils, and phenolic chemicals [223]. SCW extraction has several benefits over previous extraction processes, including reduced extracting agent costs, shorter extraction periods, improved extract quality, and an environmentally benign methodology [224].

10. Conclusions

This review article comprehensively summarizes non-edible and edible fruit waste utilization in the agro-food distribution chain. The food waste is created from insufficient pre- and post-harvest treatment and management processes; however, existing research indicates that these residues or by-products are abundant in phytochemical compounds such as phenolic compounds, antioxidants, dietary fibers, and enzymes, which all have a great potential for use in the food and pharmaceutical sectors. Novel extraction methods such as microwave-assisted extraction, supercritical CO_2 , ultrasound-assisted extraction, enzyme-assisted extraction, and other green methods can extract bioactive ingredients from wastes and byproducts. Suitable techniques are applied to bio-transform these residues into valuable materials with cheap pricing and great nutritional potential. Unquestionably, the incorporation of leftovers not only eliminates disposal issues but also eliminates pollution-related issues. As a result, additional governmental mandates and primary funding are required to put these beneficial items into the commercial sector.

Author Contributions: Conceptualization, A.A., S.R. and M.F.M.; Writing—original draft preparation, A.A., S.R. and M.F.M.; Tables and figures preparation, A.A., S.R., M.W.I., A.R. and T.M., Writing—review and editing, A.S. and N.N., supervision, X.-A.Z., M.F.M. and N.N. All authors have read and agreed to the published version of the manuscript.

Funding: The authors want to acknowledge the support of Guangdong Provincial Key Laboratory of Intelligent Food Manufacturing, Foshan University, Foshan 528225, China (Project ID:2022B1212010015).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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