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Agricultural Waste: Environmental Impact, Useful Metabolites and Energy Production

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Sustainable Development and Biodiversity

Volume 31

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Preface

With the increasing population, demand for food to quench hunger has risen. This causes pressure on natural resources like land, water, and environment. The recent standoff between two European countries further added food shortage, creating a food crisis. There are several countries facing the difficult task to feed their population, and the situation is very grave in certain countries of the Middle East and Africa. This situation has also demonstrated that food can also be used as a weapon to twist the arm. Consequently, attention is required to balance food production with disposal of agriculture waste of all sorts.

Agriculture waste is produced at various stages of food production and processing which includes disposal of residual crops, preparation of land by destroying and burning residues, waste generated by agriculture produce like husk, seeds, and leaves, use of chemicals as fertilizers and insecticides, and disposal of waste after processing fruits, vegetables, oil seeds, dairy, fish and seafoods, poultry waste, etc.

This book is a timely compilation of topics on the entire gamut and agricultural waste production and its utilization for value-added products. The book is divided in four parts: **Part I: Agricultural Waste: Environmental Sustainability, Part II: Processes for Value Addition to Agricultural Waste, Part III: Bioactive Metabolites from Agricultural Waste, Part IV: Recent Advancements, Energy and Nanomaterials from Agricultural Waste** containing 21 chapters on environmental effect to soil improvement, use of agriculture waste for processing and production of primary products like pectin, collagen, peptides, processing of tea, coffee, tomato, guava, olives waste, sugarcane bagasse, and valuable secondary metabolites from grapes, olives, wine and cider, hydrosols, and green extraction techniques, as well as recent technological advancement for the beneficial use of such by-products from agriculture such as biofuels.

The book will be useful for all those involved in environment protection, disposal of agricultural waste, rural economy, production of useful metabolites and energy. The editors wish to thank all the international contributors who have put their time to

our disposal and made serious efforts to put all the latest information in one place for this book. We are also thankful to the staff at Springer editorial and production house for their professional support.

Udaipur, Rajasthan, India — K. G. Ramawat
Villenave d'Ornon, France — Jean-Michel Mérillon
Udaipur, Rajasthan, India — Jaya Arora
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Part I
Agricultural Waste: Environmental Sustainability

Chapter 1
Disposal of Agricultural Waste and Its Effects on the Environment, Production of Useful Metabolites and Energy: Potential and Challenges

Jaya Arora, K. G. Ramawat, and Jean-Michel Mérillon

Abstract Agricultural waste and by-products are generated by all activities related to cultivation of crops; vegetable and fruit production and processing; and dairy, poultry, aquaculture and meat production associated with intensive agriculture practices and use of fertilizers. Management of crop residue requires reliable forecast about crop residue to be generated in each season/crop-wise and related policies of the government to handle this biomass. The ever-increasing world population requires increased food and fodder supply which results in increased agricultural waste biomass production. If this biomass is efficiently and wisely used for obtaining value-added products and useful material, this will not only utilize this surplus biomass but also solve many problems of pollution and simultaneously increase the income of farmers. Instead of burning and releasing sequestered carbon in the atmosphere, biomass can be channelled to useful products like antioxidants, charcoal, polysaccharides, peptides, polyphenolics, fertilizer, compost, animal feed and biofuels and developing various technologies for composite materials and innovative uses. A significant quantity (~30%) of food produced globally (1.3 billion tonnes) is wasted due to one or the other reasons, particularly of fruits and vegetables as compared to cereals, root and tuber crops, dairy, beverages, etc. Proper utilization of available resources will solve many socio-economic as well as environmental problems and help in improving living of people in rural areas particularly in developing countries. Plant-based residue or biomass generated by agricultural activities and agriculture-based industry is briefly presented as problem, and remedial measures are required for the benefit of both environment and farmers. In this

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chapter, we have discussed briefly the impact of agricultural waste on the environment, obtaining useful metabolites and products from it, and emerging novel technologies.

Keywords Agricultural waste · Agroindustrial waste · Value addition · Useful metabolites · Products from agriculture waste · Pollution · Nanomaterials

1.1 Introduction

Agricultural wastes are defined as the residues from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops (Obi et al. 2016). This agricultural waste is generated by all activities related to cultivation of crops; production of vegetables and fruits, dairy, poultry, aquaculture and meat; and use of intensive agriculture practices and fertilizers. Instead of burning and releasing sequestered carbon in the atmosphere, biomass can be channelled to useful products like antioxidants, charcoal, polysaccharides, peptides, polyphenolics, fertilizer, compost, animal feed and biofuels and developing various technologies for composite materials and innovative uses (Fig. 1.1). Even after utilizing crop residues for different purposes, about 30% (~234 million tonnes/year) is available as surplus in India (Devi et al. 2017). It is consequential that, ever-increasing population require increased food and fodder supply and resultantly increased agricultural waste biomass production. If this biomass is efficiently and wisely used for obtaining value-added products and useful material, this will not only utilize this surplus biomass but also solve many problems of pollution and simultaneously increase the income of farmers. Recently, the circular bioeconomy is gaining momentum which can offer reliable methods to reuse the organic wastes and minimize the

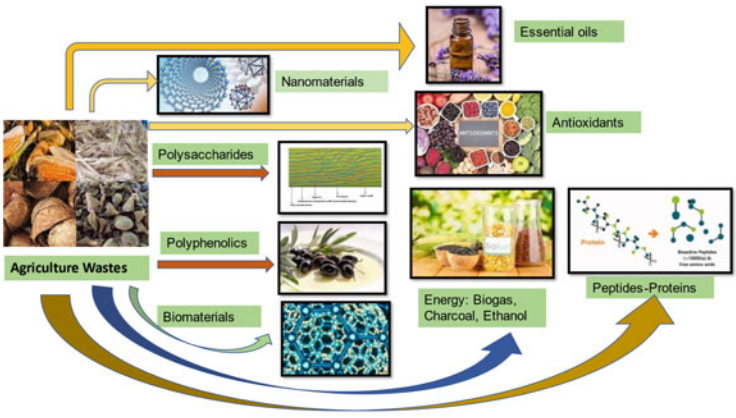

Fig. 1.1 Scope of agriculture waste in obtaining value-added products. The schematic was created using public domain images obtained from open-source database

pressure on traditional sources (Awasthi et al. 2022). In this chapter, we have discussed briefly the impact of agricultural waste on environment and possibility of obtaining useful metabolites with the help of novel technologies as depicted in Fig. 1.1. Details about these products are given in different individual chapters, hence very briefly presented here.

1.1.1 Population Growth and Demand for Food

World population is increasing at a steady rate and likely to cross 9 billion marks in 2050 or 11 billion marks in 2100 (Koop and van Leeuwen 2017; Vollset et al. 2020). Overall, the world's population is three times higher than it was in the mid-twentieth century. Though the growth rate is declining, the global population is still increasing (United Nations Department of Economic and Social Affairs, Population Division 2022, Fig. 1.2). For ever-increasing population with higher food demands, intensive agriculture is being used to produce higher crop yields per hectare and resultantly higher agro-waste. This biomass requires proper management and disposal to avoid many problems. Food consumption is measured as kcal/person/day to assess the evolution of the world food situation and social status. This consumption is increased to ~2800 kcal/day/person in the last three decades associated with

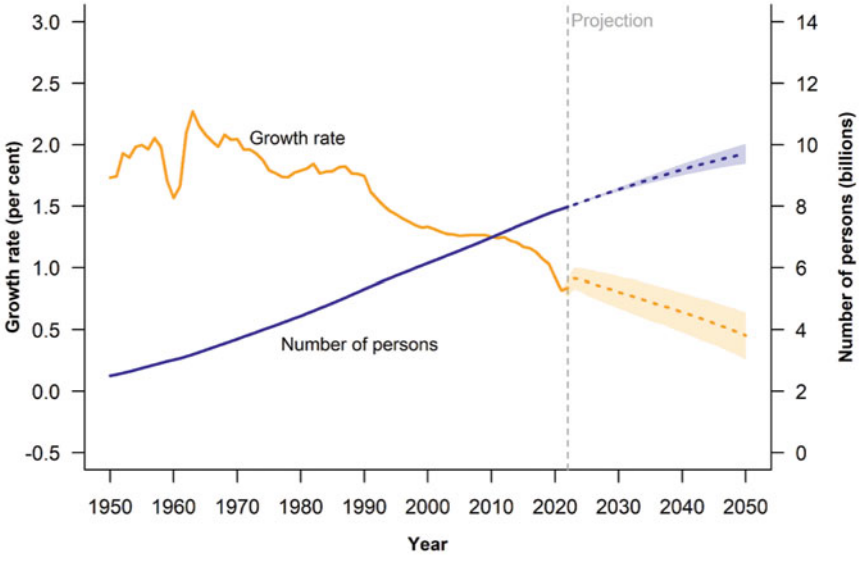

Fig. 1.2 World population and suggested increase in billions during 1950–2050 along with growth rate (United Nations Department of Economic and Social Affairs, Population Division (2022). Figure is reproduced under a Creative Commons license (CC BY 3.0 IGO) http://creativecommons.org/licenses/by/3.0/igo/)

increased population (Alexandratos and Bruinsma 2012). Tremendous pressure is exerted on all available resources to produce optimally to feed this population.

The world population is increasing, particularly in developing countries associated with poverty and unhygienic conditions. All efforts to improve the living conditions are rendered useless due to this population explosion, and to meet the challenge of feeding this hungry population is a herculean task for the agriculture scientists. After World War II, Food and Agriculture Organization (FAO) was created to tackle the problem of hunger and food supply worldwide. The development of dwarf varieties for rice and wheat contributed significantly to increasing the food grain production, particularly in developing countries like India and Mexico (Duque-Acevedo et al. 2020). To achieve SDG2 (Sustainable Development Goal 2; zero hunger) with this ever-increasing population is a challenging task for farm scientists. The balance between nutritious food production and farmer income is also an important factor (Esquivel et al. 2020). Integration of principles of agroecology, organic agriculture and regenerative agriculture is an important concept to develop a sustainable agriculture to feed this population (Giller et al. 2021). Population growth control with efficient management of agroindustrial waste is the need of hour. Therefore, sustainable utilization of all available resources is required.

1.1.2 Impact on Global Warming

Like many developmental activities, agricultural activities are also responsible for causing environmental pollution. Agriculture and agriculture-based industries produce enormous biomass which results in various types of pollution problems. Burning of straw after kharif crop harvest, particularly in Northern India, reached at an alarming state. The use of pesticides and fertilizers and the use/release of water and waste generated by agricultural activities are responsible for pollution of soil, water and environment. The challenge has become difficult in changing environment due to global warming and situation like the recent pandemic. The production of sufficient food grains consumes about 30% of energy produced which consequently impacts global warming. This results in endless cascade of events leading to harmful impacts on soil, water, energy and human health. Increasing the renewable energy crops (biomass, charcoal, energy) competes with land usage for food crops, and a balance between the two is required (Gontard et al. 2018; Joshi et al. 2019). Agricultural activities lead to global warming by promoting various gases like carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) release in the atmosphere. This has direct effect on pollution and global warming. The world consensus has developed to reduce carbon dioxide emission to 6000 megatons by 2030. Similarly, India and China have agreed to reduce methane production in rice fields by 26%. Therefore, disposing this agro-waste in eco-friendly manner will mitigate the pollution and global warming by using the biomass for the production of biofuel (biodiesel, bioethanol, biogas, biohydrogen) and bioenergy and valorization of lignocellulosic residues by producing value-added products like biofertilizers,

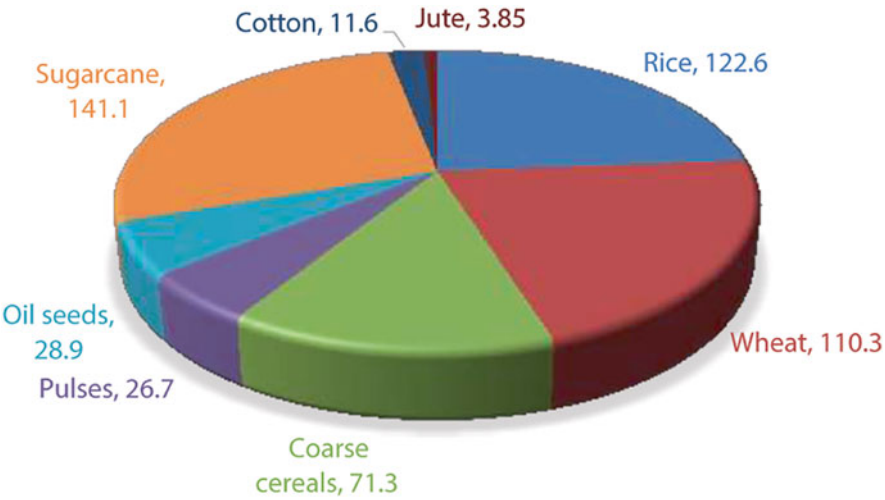

Fig. 1.3 Total crop residue generation in India; million tonnes per year. (Based on data from Devi et al. 2017)

bio-bricks, bio-coal, bio-plastics, paper, industrial enzymes, organic acids, etc. (Elbasiouny et al. 2020; Koul et al. 2022).

The total crop residue accounts for almost 50% of crop biomass produced which is far greater than any other biomass like wood, municipal waste, etc. (Elbersen et al. 2012). In developing countries like India, holdings are small, and technological inputs for cultivation as well as utilization of residual biomass are low. This results in utilization of crop residue mostly for animal feed or burning resulting in increased pollution. Biomass residue generated in India for principal crops and residue burnt are given in Figs. 1.3 and 1.4. Because of this abundance of available biomass, research activity about its utilization has increased exponentially in the last decade as reflected in surge in publications (Duque-Acevedo et al. 2020). Being large agricultural countries, most of the research publications on utilization of agriculture waste were published from the USA, China and India on crops like maize and wheat. A key role in developing sustainable agriculture has come from the international regulatory framework in developing policies by various governments, who also fund for research in this direction leading to developing technology for novel products.

The major impacts of crop residue burning are as follows: (a) emission of greenhouse gases and soot particles, (b) loss of plant nutrients and biodiversity, (c) mortality of active beneficial soil bacteria, (d) loss of soil nutrients and fertility, (e) loss of flora and fauna and (f) soil hardening and erosion due to no cover. Storage and availability of carbon in soil is determined by environmental factors, transformation processes and biotic interactions such as temperature, soil moisture and water saturation, texture, topography, salinity, acidity, vegetation and biomass production (Navarro-Pedreño et al. 2021). Burning of crop residues not only sends carbon in atmosphere but also deprives soil from it. Burning of stubble in November has

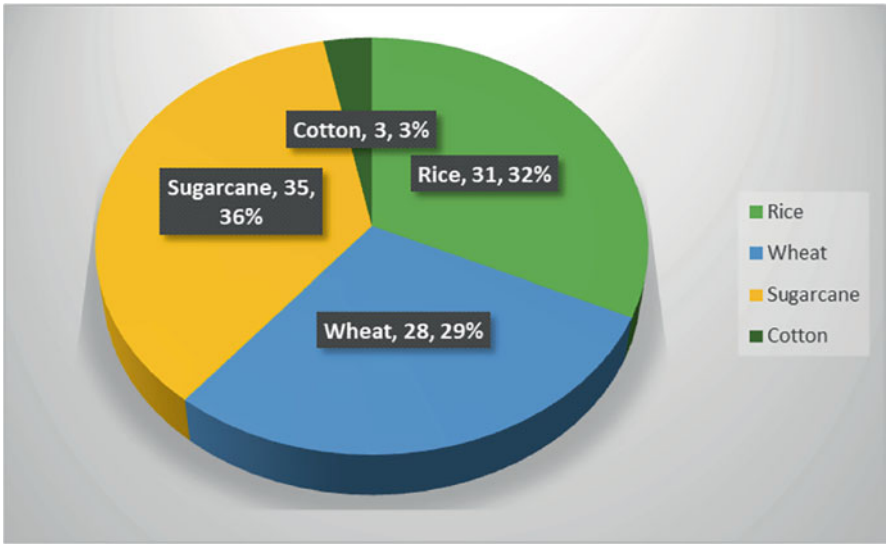

Fig. 1.4 Crop residue burnt in India; million tonnes per year

become major recurrent problem in Northern India and has become bone of contention between neighbouring states. Widespread smoke in Northern India is shown in many satellite images of NASA (Fig. 1.5). Therefore, a permanent solution of this problem is required, and alternative use of this biomass can resolve the issue.

1.1.3 Problems of Management of Residue

Management of crop residue requires reliable forecast about crop residue to be generated in each season/crop-wise and related policies of the government to handle this biomass. Since in most of the Third World countries, crops are rain-fed, forecast about rains, sowing time and seed availability are crucial for yield forecast. The by-products of crops should be used till all valuable products are not obtained and remaining residue ends up in soil. The term 'circular economy' is a model of production and consumption, which involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products as long as possible. Efficient conversion of agriculture residue into biogas and fertilizer has its own pros and cons, while obtaining useful metabolites is progressing slowing but steadily. Developing new biomaterials from agriculture waste still requires developing appropriate technology and scaling up for industrial production (Gontard et al. 2018; Capanoglu et al. 2022). Complete utilization of agriculture residues in the content of circular economy requires cost-effective and eco-friendly biotechnological methods to utilize products in food, feed, cosmetics and nutraceutical and even health (Costa et al. 2020). Similarly, much of agroindustrial biomass is generated

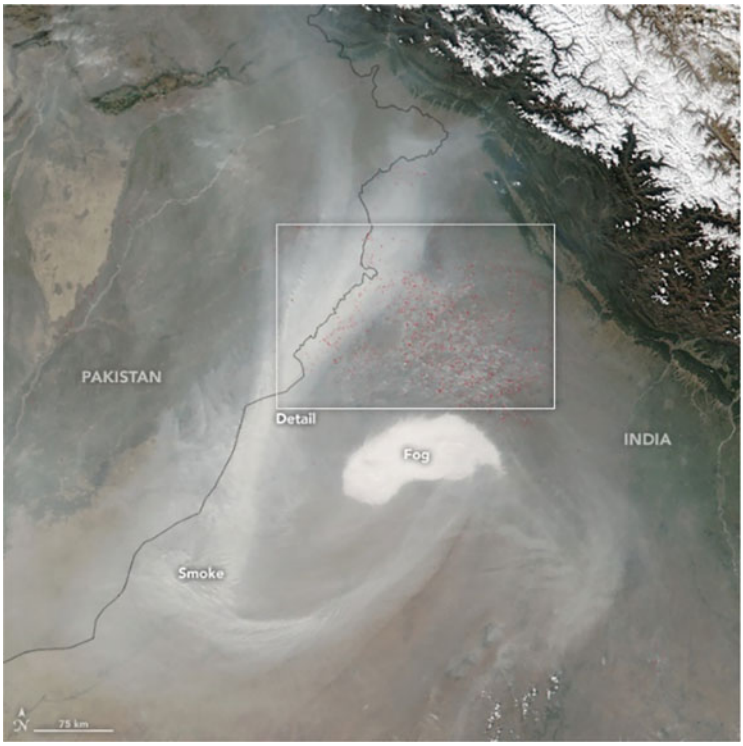

Fig. 1.5 Satellite image showing burning of residual crop (stumps in rectangle) in the fields in Punjab state and smoke and fog pollution in the entire Northern India. (Image courtesy NASA VIIRS image 2017)

from sugarcane industry and fruit and vegetable processing, canned juice production, fruit jam and jelly production and during production of dehydrated fruits and vegetables. These by-products need rapid disposal to avoid further degradation. Conventionally, fruit waste is used for animal feed, as fertilizer and compost. However, new technologies are being developed to obtain useful metabolites from this freely available biomass (see chapters in Parts II and III in this book).

1.2 Agroindustrial and Food Waste and By-Products

A significant quantity (~30%) of food produced globally (1.3 billion tonnes) is wasted due to one or the other reasons, particularly of fruits and vegetables as compared to cereals, root and tuber crops, dairy, beverages, etc. Europe alone produces more than 12 million tonnes of fruit discard every year (Ibarruri et al. 2021). Looking at the 2050 proposed data, increase in population associated with increased food production will result in higher amount of food waste biomass, and it

is of utmost importance to utilize this biomass by developing appropriate technology now, which will be perfected and industrialized in the coming decades. Most of the food waste of all types is used for the animal feed or producing compost. If this biomass is used for the extraction of value-added products like essential oils, polyphenols, anticancer compounds, pigments and enzymes or focused on the production of new foods and single-cell protein (SCP), it will impact rural economy (Wadhwa et al. 2013; Rao and Rathod 2019). A selected examples of various and diverse products including speciality chemicals are presented in Table 1.1. The examples shown are from crops, fibre crops, fruits and animal products. Therefore, availability of biomass and developing appropriate technology should be blended to develop high-value products.

Fruit and vegetable processing industries generate large quantities of biomass which is used in compost making and oil and protein extraction depending on the crop and type of fruit processed. If left unattended, it creates pollution and foul odour problems. Microorganisms, particularly fungi, play an important role in conversion of this biomass using solid-state fermentation process as compared to bacteria and insects. Fungi have advantages like high protein content, low nucleic acids and easy penetration and harvest as compared to other organisms (Ibarruri et al. 2021).

1.3 Value-Added Products

Plant cells produce two types of metabolites called primary and secondary/specialized metabolites. Primary metabolites are those which are directly involved in the metabolism like carbohydrates, lipid and proteins where secondary metabolites are end products of primary metabolism such as alkaloids, polyphenolics, terpenes, etc. (Ramawat 2019; Ramawat et al. 2009). After obtaining product of commerce, leftover biomass can be utilized to obtain these metabolites which will eventually lead to value addition to the agriculture produce or industrial process. Each cell of the biomass may contain various protein/peptides, essential oils, resins, polyphenolics or antioxidants. These compounds vary in their chemical nature and present in small quantities, which require specialized techniques to isolate these products (Ramawat and Arora 2021). The bulk of biomass can be reduced to high-value product of small volume facilitating easy handling and reduced transport cost. These include various cell wall components and their derivatives like polysaccharides and alcohols, proteins and peptides, composite produced from these, lignin degradation products and different classes of secondary metabolites, like phenolics, terpenes, alkaloids and pigments (Jimenez-Lopez et al. 2020; Meena et al. 2022). The use of agriculture waste for obtaining high-value products may have many beneficial effects on the environment, sustainable utilization of resources and improvement of socio-economic standards of farmers (Chiocchio et al. 2021).

Table 1.1 Selected examples of commercially viable products obtained from agricultural residues (Anonymous 2020; Kumar et al. 2017; Sadh et al. 2018)

S. No.	Residue/crop	Value-added/recovered products	Benefits/remarks
1.	Agricultural biomass	Biochar by using pyrolysis	Improve soil fertility and crop yield
2.	Almond hull	Pectin, phenolics, pullulan, SCP	Bioactive molecules
3.	Apple: Peel and pomace	Phenolics (epicatechin, catechins, anthocyanins, quercetin glycosides, procyanidins), biochar, biofertilizer, organic acid and enzymes	Bioactive molecules, biofuel, biomethane, bioethanol
4.	Banana, stem and peduncle	Cellulose	Ferulic acid is produced from fibre; value addition
5.	Cashew; 7mMT of cashew apples	Apple powder	Long shelf life, additional income to farmers
6.	Citrus peel	Hesperidin, naringin, eriocitrin, narirutin, galacturonic acid	Bioactive molecules, bioethanol, mucic acid
7.	Cherry pit waste	Cherry waste biomass	Biochar
8.	Crop residues, city waste and horticultural wastes	Phospho-sulpho-nitro (PSN) compost	Improving crop production, soil biological activities and overall soil health
9.	Grapes, pomace, seeds	Phenolics (dihydroxyphenols, vanillic acid, proanthocyanidins, quercetin 3-*o*-glucuronide, quercetin, resveratrol)	Bioactive molecules, value addition
10.	Groundnut shell	Cellulose by using enzyme (up to 70%), biodiesel, bioethanol, nanosheet	Import substitute, rural economy
11.	Kinnow peel	Beverage with nutraceutical properties	Alcoholic beverage with higher nutraceutical properties, proper waste utilization
12.	Kiwi bagasse, skin, seeds	Vitamins, minerals, phenolic compounds	Food, cosmetic and pharmaceutical industry
13.	Lac dye	Anthraquinone (laccaic acid A, B, C, D and E)	Pollution control, as dye
14.	Low-grade jute fibre	Handmade paper/paper board	Impact on deforestation, pollution, rural economy
15.	Lasora (*Cordia myxa*)	Polysaccharide	Value addition
16.	Livestock keratin waste	Protein	Animal feed, biosorbents
17.	Mango, peel and kernels	Antioxidants, pectin and dietary fibre, gallic acid, ellagic acid, gallates, gallotannins, condensed tannins	Value addition, stable antioxidants
18.	Oilseed cakes/meals (example soy meal, groundnut cake)	Protein isolates/concentrates	Value addition, availability of protein

(continued)

Table 1.1 (continued)

S. No.	Residue/crop	Value-added/recovered products	Benefits/remarks
19.	Oyster mushroom	Mushroom cultivation waste	Biocompost, plant growth media, bioenergy, biofertilizers
20.	Potato peel	Amylase, protease, gallic acid, caffeic acid, vanillic acid	Value addition
21.	Pomegranate: Peel and pericarp	Gallic acid, cyanidin-3,5-diglucoside, cyanidin-3-diglucoside, delphinidin-3,5-diglucoside, ellagitannins	Bioactive molecules, value addition,
22.	Rice bran	γ-Oryzanol, bran oil	Bioactive molecules, edible oil, value addition
23.	Shrimp, lobster and crab shells	Glucosamine hydrochloride is a high-end nutraceutical	Value addition
24.	Shrimp processing wastes	Astaxanthin: Carotenoidpigment	Value addition
25.	Soybean (okara: Tofu and soy milk production)	Protein	Eco-friendly disposal of soyprocessing, animal feed
26.	*Sesame* capsule	Pectin	Commercial emulsifier
27.	Tomato waste	Carotenoids	Antioxidants

Table 1.2 Examples of potential of various agricultural wastes for its utilization

S. No.	Agricultural waste	Potential utilization
1	Rice husk ash and charcoal	Additive in cement mix, active carbon
2	Rice husk	Fuel for electricity production
3	Banana peel, sugarcane fibre	Paper making
4	Oil palm fruit residue	Compost, mulching
5	Oil palm stem, rubber plant wood	Particle board
6	Husk, bagasse	Mushroom cultivation
7	Bagasse, discarded banana	Ethanol production, animal feed
8	Husk, bagasse, dung	Biogas, electricity, charcoal
9	Tea waste	Oyster mushroom cultivation

1.4 Valorization of Agroindustrial Waste

Some examples of potential direct utilization of agroindustrial waste are presented in Table 1.2. Some of them are conventionally used, while other technologies are being developed. Besides direct use of agroindustrial waste in different products, selected biomass can be used for obtaining value-added primary metabolites and secondary metabolites.

1.4.1 Various Useful Primary Metabolites Obtained and Processes

All plant tissues are mainly made up of lignocellulose, whereas animal tissues are made of proteins and lipids. Cellulose is the highest plant-based molecule on the planet Earth (chitin from animal world). Huge biomass is generated as crop residue or during processing of fruits and vegetables for direct consumption or for drying, canning, pickles, jams and jellies and juices. Such a discarded plant and animal waste is available for extracting useful primary metabolites such as cellulose, pectin, lignocellulose, peptides, enzymes (amylase, cellulase, pectinase, invertase, xylanase), developing composite, etc., from plants. In animal system, all available resources are utilized for obtaining products like chitin, collagen and whey products. In all these cases, handling, transporting and extracting huge biomass are a costly affair; hence, ancillary industries need to be set up in the vicinity of main food processing industry.

1.4.2 Various Bioactive Secondary Metabolites Obtained

Those secondary metabolites which exert a profound physiological effect in a mammalian system are known as medicinal or bioactive compounds. As stated above, these compounds are present in small quantities in all plant parts, and depending on the type of residue, the chemical nature of these compounds is also diverse. On the basis of their biosynthesis, these are broadly classified as alkaloids, terpenes and phenolics. Some selected examples of bioactive compounds obtained from different industrial food waste residues are presented in Table 1.3.

We have not discussed in detail the individual plant or process here, but a general view is presented. There are several well-known and established agricultural and horticultural crops like *Vitis* (canes, pomace, seeds, skin), olives (branches, leaves, seeds, pomace), mango (fruit peel, seeds), orange (peels, pulp residue), apple (pomace), cashew (cashew apple botanically pedicel), wall nut (shell) and various parts of tea, coffee and cacao, where huge biomass is generated during cultivation and fruit processing (Sadh et al. 2018; Malenica and Bhat 2020; Chiocchio et al. 2021). Enormous residue (peels) generated during fruit processing of tomato, banana and citrus is used for obtaining carotenoids, phenolic acids, flavonols, catecholamines and essential oils, respectively. There is no common method or process to treat this biomass, and based on chemical nature, a method is adapted, for example, water (solid-aqueous phase extraction) for water-soluble compounds like neutral alkaloids or slightly acidic or basic aqueous extraction for some alkaloids or phenolics. Essential oils are steam distilled, whereas other products may be extracted using microwave-assisted, supercritical fluid extraction or pressurized liquid extraction methods (Sadh et al. 2018; Chiocchio et al. 2021). Another approach to obtain useful metabolites is the use of solid-state or liquid-state fermentation by the use of

Table 1.3 Some selected examples of bioactive compounds obtained from different industrial food waste residues (Kumar et al. 2017; Sadh et al. 2018; Malenica and Bhat 2020; Chiocchio et al. 2021)

S. Nos.	Source residue	Bioactive components
1.	Apple peel and pomace	Epicatechin, catechins, anthocyanins, quercetin glycosides, chlorogenic acid, hydroxycinnamates, phloretin glycosides, procyanidins
2.	Beans	Several isoflavonoids, daidzein, genistein
3.	Carrot peel	Phenolics, carotenoids (beta-carotene, alpha-carotene, etc.)
4.	Citrus fruit peel	Hesperidin, naringin, eriocitrin, narirutin
5.	Coffee beans	Polyphenols (several isomeric caffeoylquinic acids, dicaffeoylquinic acids, feruloylquinic acids and epicatechin, considered as potent antioxidants)
6.	Grape seed and skin	Coumaric acid, caffeic acid, ferulic acid, chlorogenic acid, cinnamic acid, neochlorogenic acid, *p*-hydroxybenzoic acid, protocatechuic acid, vanillic acid, gallic acid, proanthocyanidins, quercetin 3-*o*-glucuronide, quercetin, resveratrol
7.	Green tea	(−)-Epigallocatechin, (+)-gallocatechin, (−)epicatechin-3-*O*-gallate
8.	Guava skin and seeds	Catechin, cyanidin 3-glucoside, galangin, gallic acid, homogentisic acid, kaempferol
9.	Litchi pericarp, seeds	Cyanidin-3-glucoside, cyanidin-3-rutonoside, malvidin3-glucoside, gallic acid, epicatechin-3-gallate
10.	Mango kernel	Gallic acid, ellagic acid, gallates, gallotannins, condensed tannins
11.	Olives	Anthocyanins (cyanidin and delphinidin glycosides), flavanols, flavones, phenolic alcohols (tyrosol, hydroxytyrosol), secoiridoids (oleuropein)
12.	Pomegranate	Gallic acid, cyanidin-3,5-diglucoside, cyanidin-3-diglucoside, delphinidin-3,5-diglucoside, ellagitannins
13.	Potato peels, tomato residues	Glycol-alkaloids
14.	Tomato skin and pomace	Carotenoids (lycopene)
15.	Wheat bran and germs	Phenolic acids, antioxidants

microorganisms. Several species and strains of bacteria and fungi are used for this purpose (Ibarruri et al. 2021; Sadh et al. 2018). Microbial degradation and value addition to the agriculture waste is at the forefront due to sustainable approach (Singh and Singh 2022). Metabolomic profiling of agricultural waste with the help of available high-throughput analytical techniques, such as high-performance liquid chromatography, gas chromatography, mass spectroscopy and NMR, has resulted in isolation and characterization of various bioactive metabolites (Khaksar et al. 2022). The products obtained by such processes provide valuable drugs and therapy products or are used for fortification. As the bulk of biomass is available free/at low cost, commercial viability of the project and products is always high.

1.4.3 Composting of Agrifood Wastes

Agricultural and food wastes are increasing because of high yield of cultivars, technological inputs and feeding increasing population which create pressure on the environment due to methane gas and pathogenic microorganism causing health hazards by reaching ground water and fields. Food waste is a significant contributor to the greenhouse gases and consequently global warming (Al-Rumaihi et al. 2020). Therefore, microorganisms in the composting can be effectively monitored by using modern techniques of molecular marker like biochemical identification, polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE), terminal restriction fragment length polymorphism (T-RFLP), single-strand conformation polymorphism (SSCP), microarray analysis and next-generation sequencing (NGS) (Palaniveloo et al. 2020).

Traditionally, recycling technologies use this waste for landfills, incineration and composting. The use of agriculture waste and food waste can be used for making compost, which is in practice since a long time, but it is generally a local process. Composting requires a close monitoring of the process, and depending on the ingredients, the presence of harmful heavy metals may be a problematic issue. Composting can be improved by various processes and methods like co-composting, addition of inorganic/organic additives, reducing gaseous emissions and use of different microbes (Awasthi et al. 2020). Details of various methods and microorganisms involved can be found elsewhere and are beyond the scope of this chapter (Maheswari 2014).

The degradation of soil quality and fertility due to intensive use of nitrogen fertilizers, industrialization and human activity has resulted in finding ways to improve soil quality (Verma et al. 2022). Biochar has been shown to effectively counterbalance deteriorating soil conditions by way of waste management, C sequestration, reduction of greenhouse gas emission, water and soil remediation and enhancing soil fertility and crop production. The use of biochar produced from agro-waste along with or without organic manure in the field has positive response in amelioration of soil quality and plant growth (Zhou et al. 2022; Haider et al. 2022). However, this is the beginning, and more research data are required before a final conclusion is drawn. More details are given in Chap. 2 in this book.

1.4.4 Renewable Energy Production

Renewable bioenergy like biogas, biodiesel and ethanol can be produced from available agriculture waste without increasing the cultivation land area for energy crops. Consequently, this will also reduce the methane generation if this waste is used for energy production instead of landfills. The use of biodiesel and ethanol in petroleum diesel is priority area in most of the countries to reduce dependence on continuously depleting fossil fuel (Sharma et al. 2017). Agricultural and food waste

is mainly composed of lignocellulose (1.5×10^{11} tonnes/annum), and appropriate technology can convert this into ethanol (see Part IV in this book). This lignocellulose has to be converted by hydrolysis into simple sugars so that these sugars are fermented to ethanol by microorganisms (Joshi et al. 2020, 2021). Therefore, technical improvement of hydrolysis, inhibitory effect of residual acids/chemicals, selection of microorganisms to convert pentoses, etc., are major bottlenecks in efficient conversion process of agricultural waste into bioethanol, biobutanol, biogas, biohydrogen and biodiesel (Pattnaik et al. 2019; Panpatte and Jhala 2019; Joshi et al. 2022). Agro-waste biorefineries result in zero waste and are viable, sustainable and eco-friendly processes for converting agro-waste in useful products particularly in developing countries (Dhanya 2022; Duan et al. 2022).

Crop residues, food and fruit waste disposal and waste water from such processes need to be disposed in a manner to not cause harm to water bodies and environment. Waste, by-products and effluents coming from industrial processing and agricultural procedures of vegetables and fruits can be defined as biomass, according to CE directive 2001/77 (Valentina et al. 2014).

1.4.5 Nanotechnology: An Advance Tool

Nowadays, nanotechnology has become an important green technology in valorizing agricultural waste (Capanoglu et al. 2022). Various bioactive compounds present in agriculture waste act as capping and reducing agents and accelerate the synthesis of various nanoparticles such as silver, gold nanoparticles, graphene oxide, solar grade silicon nanoparticles, amorphous silica, carbon and various metallic nanoparticles (Thangadurai et al. 2021). Bio-nanocatalysts, bio-nanosorbents made from agroindustrial biowaste, are being deployed for removing organic and inorganic water contaminants from water bodies and creating a circular economy nexus (Omran and Baek 2022; Abdelbasir et al. 2020). A method was developed using iron oxide nanoparticles from mill scale and applied them in adsorption of dye contaminants from industrial waste water. With an average-sized nanoparticles (55.76 nm), optimum efficiency (99.93%) of adsorption of dye contaminants was achieved (Arifin et al. 2017). Cellulose being abundant biopolymer of agriculture waste can be converted to nano-fibrillated cellulose; a potential biopolymer can be used for rapid drug delivery, stabilizing agent and culturing cells for tissue engineering (Kamel et al. 2020). The bioactive phytochemicals present in agriculture and industrial waste stream can be made available by nanoencapsulation using biodegradable active packaging material (McClements and Öztürk 2022). Porous silica nanoparticles synthesized from rice husk were used in purification of air, mainly removal of CO_2 (Zeng et al. 2017). Further synthesis of various nanomaterials using agricultural waste has been described in detail in Chap. 21 of this book.

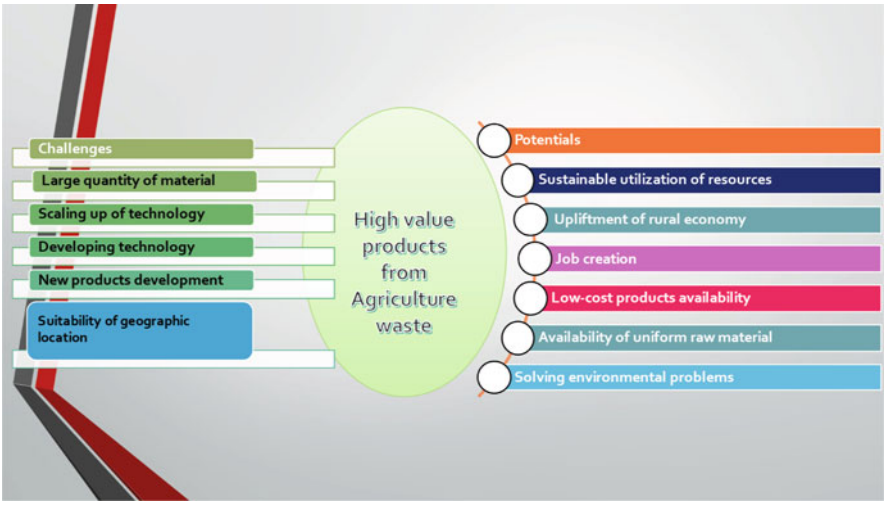

Fig. 1.6 High-value products and metabolites from agriculture waste: challenges and potential

1.5 Conclusions, Prospects and Challenges

The biomass generated by all these agricultural activities is huge, and so is the problem of its utilization and pollution. This requires new environmentally friendly technology development and then scaling up the process to industrial level. Research activities in several directions like biofuel production, biochar and soil amendments, obtaining useful primary and secondary metabolites and producing novel material and composites are priority research trends and new products are developed. In short, challenges and future prospects are presented in Fig. 1.6. It is necessary to find new products which are not available otherwise by traditional crops or methods. These challenges will resolve the problem of demand and supply and utilize the available biomass, generate new jobs and help in economic upliftment of farmers. The use of solid-state fermentation, development of efficient bacterial and fungal strains and environmentally friendly processes are the need of hour. Proper utilization of available resources will solve many socio-economic as well as environmental problems and help in improving living of people in rural areas particularly in developing countries.

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Chapter 2
Utilizing Agricultural Waste in Production of Biochar for Improving Soil Properties and Increasing Crop Yield Through Field Application

Mahendra Pratap Choudhary, H. D. Charan, and Biswajit Acharya

Abstract Management of agricultural waste has recently become a grave problem in India. The technological advancement and farm mechanization have resulted into improved crop production, but simultaneously, in the absence of practical and economic options, the farmers prefer to burn the agricultural waste in open fields which creates environmental threats in terms of emission of greenhouse gases responsible for environmental and human health hazards. The direct burning of agricultural waste also deteriorates the soil quality as well as results in loss of biomass and soil microbes leading to reduced crop yields. This burning of agricultural waste (locally known as *Parali*) in the adjoining states of Delhi is presumed to be one of the reasons for dense smog and very high air pollution in the national capital region of New Delhi after Kharif season in the months of October to November every year for quite some time. The concerned governments, the National Green Tribunal (NGT) and Hon'ble Supreme Court of India are constantly monitoring over the issue and have put it on utmost priority to find out a permanent solution of this recurring problem. With the objective of finding out an optimum solution of the problem, a novel indigenous method has recently been found out in which the disposal of agricultural waste is ensured in an eco-friendly manner by converting it into a useful product, known as biochar. The biochar has great potential in mitigating air pollution and, when applied to soils, can help in upgradation of soil properties and increased yield of the crops. The concept behind the innovation is that of the thermal conversion, in which the crop residues are subjected to pyrolysis either in little presence or absence of oxygen. The most significant feature of the method is its adaptability. The farmers can convert their agricultural waste into biochar at the fields, and the biochar so produced can be further applied to the soils for upgrading the soil properties that ultimately helps to increase the crop

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production. This novel method of producing biochar is very simple and does not require much investment and technical skills.

Keywords Agricultural waste · Biochar · Soil improvement · Crop yield

2.1 Introduction

Agriculture is the backbone of Indian economy as more than two-thirds of the Indian population is involved in some way or the other with the agriculture and associated activities. Indian farmers are nowadays making use of modern technology and farm machinery for increased crop production and faster harvesting. This has resulted into yet another issue of agricultural waste management. In order to prepare their fields for the upcoming crops, the Indian farmers usually adopt the practice of stubble burning. Due to unawareness of the modern methods of waste management and the time and resources required therein, the farmers prefer to burn the large quantities of crop residues in the fields itself. The new age harvesters and mechanical crop cutters cut and collect the useful upper half portion of the crops such as wheat, mustard and paddy and leave behind the bottom half parts in the form of stalks. As the farmers get very less time in between two crop seasons for field preparation for the upcoming crops, they burn the crop residues directly in the open fields. This practice not only saves a lot of time but also the money otherwise required to invest on clearing the fields manually or mechanically. There are some other motives of the crop residue burning in the field such as shortage of laborers and unavailability of residue buyers (Kaur 2017). At first instance, this practice may be seen as a faster and cheaper one, but in broader aspects, it proves to be very harmful for the human and the animals, the soil biota and the environment as a whole. Inappropriate clearance of biomass produced by the agricultural sector is a major environmental threat all over the world (Siddiqui et al. 2017). The burning of agricultural waste produces harmful greenhouse gases such as CO_2, CO, CH_4 and oxides of nitrogen (Gupta et al. 2004) which eventually emit in the atmosphere and cause long-term environmental impacts.

The annual incidences of very high levels of air pollution and smog during October to December months in the national capital region of New Delhi, for some years in the recent past, are allegedly known to occur because of this crop residue burning in the nearby adjoining states of Punjab, Haryana, Rajasthan, Uttar Pradesh and Madhya Pradesh (Kumar and Singh 2020). Although, way back in the year 2015, the National Green Tribunal (NGT), New Delhi, had already banned the open burning of the crop residues, leaves and such any other materials releasing noxious contaminants into the ambient atmosphere, the farmers are yet not complying it in its true sense. The gravity of the situation can be realized with an instance when the city of New Delhi observed the most dangerous state of air quality index, i.e. worst category during winter 2017 when the fine particulate matter ($PM_{2.5}$) was observed at the maximum concentration ever at 640 μg m^{-3} (ETB 2017) as compared to the allowable value of 40 μg m^{-3} as per the Indian national standards on ambient air quality (NAAQS 2009).

Bhuvaneshwari et al. (2019) discussed the issue of crop residue burning in India highlighting the socioeconomic roots behind the cause rather than agricultural or waste management concerns. They discouraged the solutions entailing high capital investments in terms of infrastructural requirements or costly technologies. The authors insisted on sustainable way-outs for crop waste minimization and utilization in the form of generating biogas and biochar as well as in situ management. More intensified mechanization in harvesting had been recommended to adopt along with subsidized provisions by the government so that the farmers can be encouraged. Kumar and Singh (2020) reviewed the responsible factors behind burning the crop residues by the farmers in India and proposed the alternatives in terms of the socioeconomic sustainability of the farmers. They concluded that in spite of burning the crop residue in fields, it must be used for production of biogas, biochar and bioethanol or as a fuel in thermal power plants.

Hence, it can be realized very well that the crop residue burning in open agricultural fields is against the established environmental norms as it burns useful biomass and at the same time gives access to harmful gases into the atmosphere. Therefore, looking to the severity and recurring incidences of stubble burning, a simple, cheaper and viable answer to the problem has been found out. An innovative way of converting the abundant crop residues into a useful product called biochar has been revealed. This method not only helps the farmers in solving the problem of clearing their agricultural fields well in time but also assists in reducing the atmospheric pollution and increasing the productiveness of the soils by stabilizing them and at the same time sustainably managing the huge amounts of crop residues.

2.2 Biochar Production

It is believed that the Amazonians first produced and used charcoal (biochar) for improving their nutrient-poor soils around 2500 years ago. They discovered to produce biochar by first igniting the biomass, then burying it in ground (or earth) and finally leaving for smoldering in the absence of oxygen. This method can be called as slash-and-char which results in carbon sequestration up to 50%, whereas the method adopted by modern farmers in India is a type of slash-and-burn which results in only 1–3% of carbon sequestration, and a high amount of ash is produced. The term biochar was first coined by Peter Read in 2005 (Godbey 2016) to illustrate a material that looks almost similar to charcoal, but that is actually carbonized biomass converted into a solid material, used to enhance functions of soil and lessen emissions of greenhouse gases. One of the earliest studies proposed the use of biochar into soils as a new method to set up a considerable and lasting storage for atmospheric CO_2 in terrestrial ecosystems (Lehmann et al. 2006).

A carbon-rich product, biochar is attained through a method known as pyrolysis. This method involves heating of biomass or other organic substances at temperatures above 250 °C either in the little presence or absence of oxygen (Lehmann 2007). The researchers are showing increased interest in biochar during the last decade because

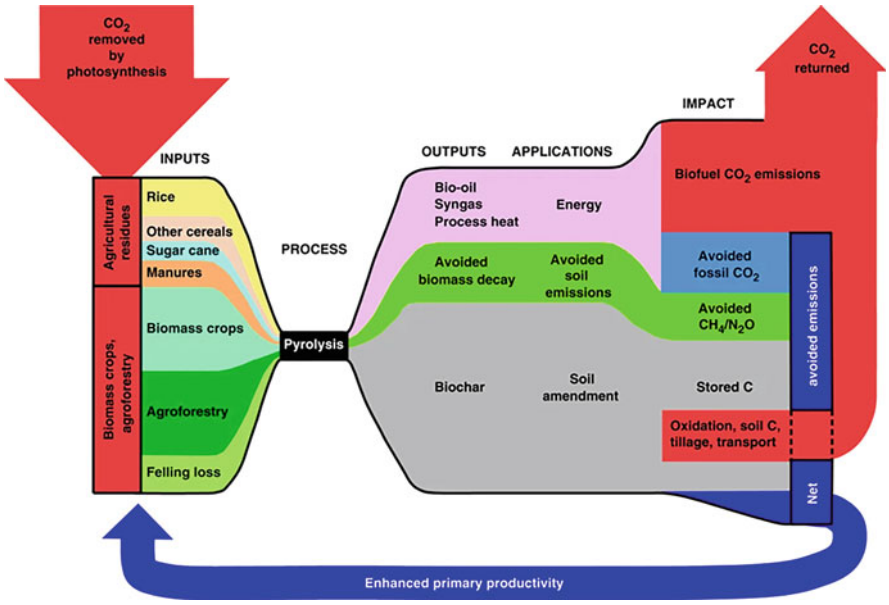

Fig. 2.1 Flowchart showing sustainable biochar concept (Woolf et al. 2010)

of its potential scope in multidisciplinary areas like mitigating climate change as well as potential for soil amendment and sustainable farming (Lehmann et al. 2011).

The concept of sustainable biochar is represented in Fig. 2.1, which shows inputs, process, outputs, applications and impacts on global climate. The height/width of the different coloured fields represents the relative proportions of individual components of each category (Woolf et al. 2010). The process starts from the removal of CO_2 from the atmosphere by photosynthesis to yield biomass. Out of this total biomass, a fraction consisting of agricultural residues, biomass crops and agro-forestry products is converted through a process called pyrolysis into biochar, bio-oil, syngas and process heat. The bio-oil and syngas are further used to get energy through combustion. This energy and the process heat generated as above are used to offset fossil carbon emissions (Woolf et al. 2010).

The biochar produced acts to store carbon for a very long period as compared to the case when biomass would have not been converted to biochar and left for decay on its own. During the process, CH_4 and N_2O emissions are significantly avoided by way of skipping natural decay of biomass. The biochar can be used to amend soils, and the CO_2 returned to the atmosphere is less in comparison to the originally produced by direct combustion of the biomass. Thus, biochar acts as carbon-negative. Another simple explanation in terms of flowchart for producing biochar through pyrolysis is shown in Fig. 2.2 in which we can see that biomass is used for production of biochar and bio-energy generation and 50% of the carbon is returned back to the soil as carbon sequestration.

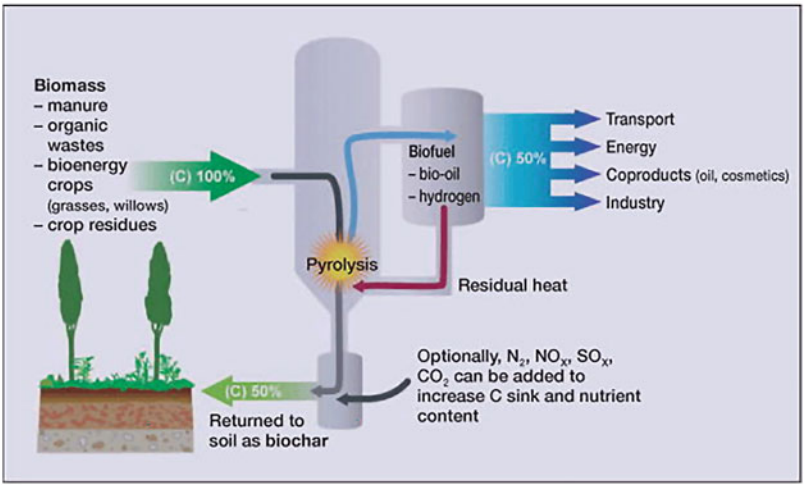

Fig. 2.2 Flowchart showing biochar production technology (Lehmann 2007)

The production methods of biochar have changed a lot over the centuries, but the principles have remained the same. These days biochar is produced in a complete eco-friendly manner through the processes called pyrolysis, gasification and hydrothermal conversion in which biomass is heated anaerobically and all the emissions are captured in the closed system and subjected to re-burn or broken down into less harmful elements, hence preventing the release of CO_2 and other GHGs into the atmosphere.

The simplest method of producing biochar is the thermal decomposition of the biomass because traditionally biomass has primarily been the raw material used to produce biochar. Biomass consists of biodegradable portions of the products, wastes and residues from agriculture, forestry and other allied agro-industries and biodegradable municipal waste also. There are two basic approaches for the production of biochar. The ancient approach consisted of either earthen pits or mounds in which the wood was piled and covered with the earth itself. Then it was burned slowly with a limited amount of air. The method is still used in some of the developing countries to make charcoal, but it produces considerable smoke and also releases CO_2 and other GHGs into the atmosphere. The modern approach is based on the concept of pyrolysis, and both small-scale and large-scale productions of biochar are carried out using biochar stoves, ovens or kilns and large industry setups. Countries like Japan, China and Australia have innovated small pyrolysis ovens which help to dispose of domestic waste and produce biochar for small gardens. The bigger size stoves can be converted into portable units so that they can be used at the site of biomass and hence transportation costs can be minimized. For large-scale production of biochar, pyrolysis reactors are established at such places where other infrastructural facilities are easily available.

Biochar can be produced from a variety of biomasses such as agricultural wastes, organic wastes, forest residues, bioenergy crops, kitchen wastes and sewage sludge having diverse physical and chemical characteristics (Nartey and Zhao 2014). It can also be produced from other waste materials like manure and green wastes which may otherwise produce even more obnoxious greenhouse gases when resorted to disposal by open burning (Lehmann and Stephen 2015). Therefore, it is advantageous to utilize such leftover materials in a more productive way. For a very long time, the production and storage of biochar in soils has been proposed as a means of climate change mitigation through carbon sequestration, providing energy and increased crop production (Woolf et al. 2010). A large number of foreign researchers are working on the aspects of biochar production and its use for soil amendment (Barus 2016; Carter et al. 2013; Ding et al. 2016; Fryda and Visser 2015; Gokila and Baskar 2015; Parmar et al. 2014; Tammeorg et al. 2016); nevertheless, there are only a few significant evidences of research on biochar in India, being comparatively a novel thought in terms of making use of crop residues for producing biochar and its application as soil amendment.

2.2.1 BioCharan*: An On-Site Method of Biochar Production*

Occurrence of a large number of crop residue burning incidences in India and the vacuum of a suitable technological solution easily adoptable by the farmers were the two actual inspirations to carry out the study (Choudhary et al. 2021a). A novel method named *BioCharan* has been developed for converting the crop residues into biochar. The method clears the agricultural fields for upcoming crops on the one hand, while, on the other hand, it helps in reducing the environmental pollution, stabilizing the field soils as well as problematic expansive soils and enhancing the physical and chemical properties of soils and eventually the yield of crops. Hence, it proves to be a perfect step towards attaining the sustainable development (Choudhary et al. 2021b). This method is an economic and feasible one as it does not require any technical skills to operate and an individual farmer can convert the residues into useful product biochar to resolve the problem of crop residue disposal and environmental air pollution through emission of greenhouse gases during crop residue burning. The studies carried out so far and available in the literature point out towards using biochar to enhance the agronomic parameters of soils related to improvement in crop yield and soil fertility. This review is supposed to be one of the leading reviews of its kind in India wherein application of biochar has been used to study the effect on geotechnical characteristics of the soils. By understanding the concept of conventional methods of biochar production and then applying some indigenous wisdom, it was considered to produce biochar at the field level through a modified kiln made up of a cylindrical empty diesel drum. Looking to the absence of any cost-efficient alternative in Indian scenario, the farmers can produce biochar using this novel method of *BioCharan*, and the biochar produced can be further utilized in the fields for increasing the soil fertility (Choudhary et al. 2021c).

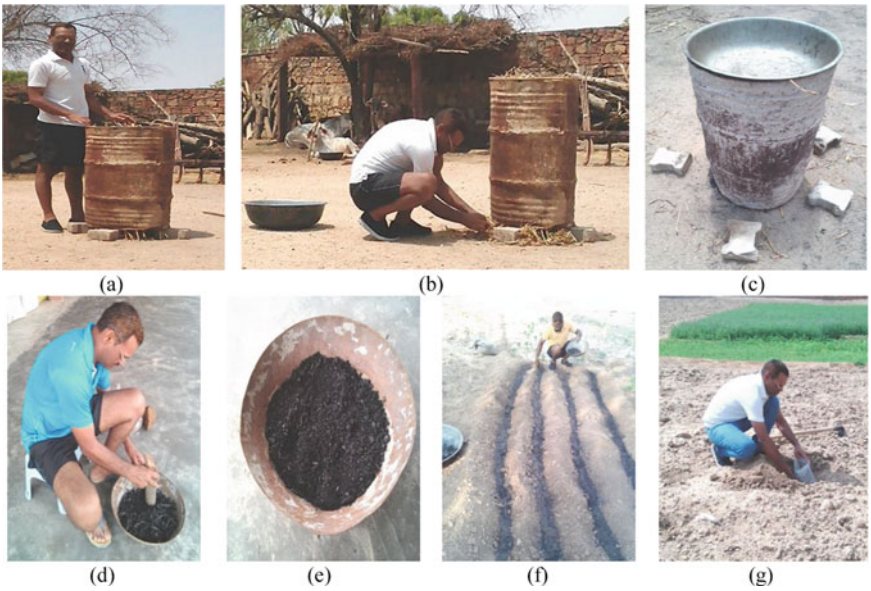

Fig. 2.3 (**a**) Drum filled with *mustard* crop residues; (**b**) burning on fire at the bottom; (**c**) drum covered with a top lid and left for 15–20 min for pyrolysis to take place; (**d**) raw biochar produced; (**e**) biochar crushed into small pieces; (**f**) applying biochar in agricultural field; (**g**) collecting soil sample

Figure 2.3 shows various steps of on-site biochar production applying the drum method and its field application as well as collection of soil samples.

A cylindrical drum having both ends open with 3 ft height and 2 ft diameter has been utilized to make biochar from crop residues. The drum is supported on stones or bricks so that limited entry of air can be ensured from the bottom end. The drum is then filled up with the crop residues, and, once filled, it is ignited at the bottom. After ignition, the residues are allowed to burn only for 2–3 min, and the supporting stones or bricks are taken away, and the drum is covered at the top with a lid. The crop residue inside the drum is hence allowed to convert into biochar through heating process for a period of about 10–15 min. The drum is then detached from its position when it becomes cool, and the raw biochar is collected and crushed into smaller parts so as to mix with soil samples either for laboratory experimentation or for field trials.

A drum can process crop residues of about 15–20 kg at a time. Therefore, it is advisable to use five to six such drums at the same time so that about one quintal of agricultural waste can be transformed into biochar at an instance, i.e. 15 min. In this way, one ton of crop residues can be produced in about 3 h. The overall cost of converting the crop residues into biochar comes out in the range of Rs. 4–5 per kg considering the costs involved in cutting of the residues up to the final production of biochar (Choudhary et al. 2021d). Hence, the production cost of biochar is quite less as the method does not necessitate any expensive equipment or technical skills.

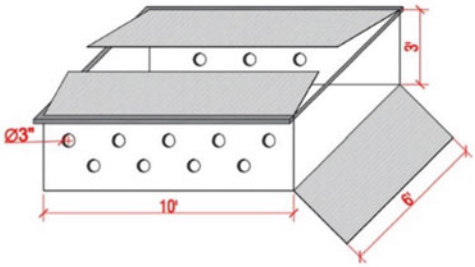

Fig. 2.4 Three-dimensional view of the *biochar trolley*

The volume of the drum is approximately 9.43 cubic feet (0.27 m^3) only which is quite less, and proper compaction is also required during filling up; otherwise, voids will remain in it. In this way, a large number of drums are required simultaneously to convert the available crop residues into biochar. Therefore, to further optimize the method of *BioCharan*, a modified design of tractor mounted trolley has been proposed as shown in Fig. 2.4. The conventional tractor trolley has the dimensions of 10′ × 6′ × 1.5′ which has been proposed to have new dimensions of 10′ × 6′ × 3′, i.e. only the height of the trolley has been increased so as to double the volume of the trolley without causing any other practical hindrances in its operation. The volume of the modified trolley is 180 cubic feet (5.09 m^3) which is approximately 19 times more than that of the drum. Hence, it increases the rate of conversion of crop residues into biochar and proves very economical as compared to the drums. The bottom face of the trolley is provided with two circular openings having adjustable covers/caps of 1 foot diameter so as to allow easy collection of raw biochar directly beneath the trolley.

This trolley acts as a *biochar trolley* as and when required; otherwise, it is a normal trolley with double the capacity of the conventional tractor trolley. The other modifications include provision of small holes of 3″ diameter having caps on both the sides of the trolley at suitable intervals so as to facilitate easy escape of smoke and gases during the process of pyrolysis, if required. To convert the trolley into a closed system, provision of top cover has been suggested in the form of additional sliding walls of 3′ height on both sides so that, when required, they can be raised above to close the trolley at the top. During normal functioning, the top cover splits into two-halves and stands inside the side walls and hence does not cause any obstruction.

2.2.2 Soil Preparation and Experimental Setup

In an experimental study, the soil samples were collected from fields, wrapped in polythene bags and taken to the soil testing laboratories for further processing where they were prepared as per the methods and procedures prescribed by the Bureau of Indian Standards (IS: 2720 1983). At the outset, the soil samples were placed in

thermostatically controlled oven for drying, then pulverized and finally sieved through 4.75 mm size sieves. The particle size analysis, soil classification and other soil characteristics were found out as per the relevant IS standards. The soil type was classified as CI (inorganic clay having intermediate plasticity) according to the Indian Standard Soil Classification System (Choudhary et al. 2022). All relevant experiments were carried out in the laboratories to work out the outcome of mixing biochar on the physicochemical and engineering properties of the soil. The samples of soil were mixed with varying proportions of biochar by weight (% w/w) starting with minimum 5% and then increasing in its multiples up to maximum 25%. The biochar was added to soil in dry form ensuring that both are mixed thoroughly.

2.2.3 Biochar Characterization

Xie et al. (2016) summarized the biochar characteristics produced from different feedstock and identified the potential of biochar to maintain soil quality and sequester carbon. They analysed the biochar properties in reference to the sources of biochar considering elemental compositions, pH, surface area and cation exchange capacity. They found biochar technology as the right approach for neutralizing carbon resulting from carbon storage by itself and in reducing the GHG emissions, including CO_2, CH_4 and N_2O. The authors concluded that biochar exhibited huge probability for extended use in environmental fields; nevertheless, added continuing field trials are necessary to assess biochar application rates.

2.2.3.1 Physicochemical Characteristics and Particle Size Distribution

The characterization of biochar produced using *BioCharan* method when carried out by analysing physicochemical parameters as well as particle size distribution is shown in Table 2.1.

2.2.3.2 Elemental Analysis

The CHN analysis of biochar sample is shown in Fig. 2.5. The major elements found in biochar were carbon (45.421%), hydrogen (1.839%) and nitrogen (1.095%), whereas the other minor elements like sulphur and oxygen were not found. Hence, the CHN analysis confirms that biochar samples are carbon-rich.

2.2.3.3 FTIR Spectroscopic and SEM Analysis

The FTIR spectrum shows the functional groups present in a sample. The FTIR imaging of biochar is shown in Fig. 2.6. The biochar sample has more than five

Table 2.1 Important physicochemical characteristics of biochar and soil (Choudhary et al. 2022)

S. No.	Characteristics	Biochar	Soil
1	pH	9.56	7.62
2	Specific gravity	1.84	2.56
3	Moisture content (%, at 105 °C)	16.94	11.12
4	Electrical conductivity (mS cm^{-1}, at 25 °C)	9.65	4.23
5	Organic carbon (%, as OC)	1.86	0.56
6	Organic matter (%)	2.24	0.98
7	*Particle size distribution (%)*		
	(a) 2–4.75 mm	23.6	5.4
	(b) 0.425–2 mm	43.4	17.0
	(c) 0.075–0.425 mm	30.0	27.2
	(d) 0.002–0.075 mm	2.0	26.8
	(e) <0.002 mm	1.0	23.6
8	*Consistency limits (%)*		
	(a) Liquid limit	–	43.12
	(b) Plastic limit	–	24.25
	(c) Shrinkage limit	–	17.63
	(d) Plasticity index	–	18.87
9	*Geotechnical properties*		
	(a) Optimum moisture content (%)	–	16.00
	(b) Maximum dry density (g cm^{-3})	–	1.64
	(c) Water-holding capacity (%)	–	32
	(d) Unconfined compressive strength (kg) cm^{-2})	–	1.68
	(e) California bearing ratio (%)	–	1.96
	(f) Free swell index (%)	–	39

peaks indicating that biochar is not a simple element. The spectrum shows C–H, O–H and N–H as well as S=O, C=C and O–Si–O stretching and bending vibrations in the range of 3727 to 457 cm^{-1} indicating the existence of various functional groups like phenolic, hydroxyl, methyl, methylene, alkane, alkyl and silica.

The scanning electron microscopic (SEM) analysis of biochar in Fig. 2.7 shows the spectroscopic image of biochar obtained from mustard waste biomass.

The SEM analysis is helpful in demonstrating that biochar has porous and permeable structure besides large surface area. These characteristics are responsible for increased water-holding capacity and nutrient uptake.

2.2.3.4 XRD Analysis

The XRD image helps to determine the crystalline phases in a mixture by comparing with position and intensity of reference patterns. The XRD analysis of biochar is shown in Fig. 2.8. The peaks in XRD pattern indicate the presence of graphite, SiO_2,

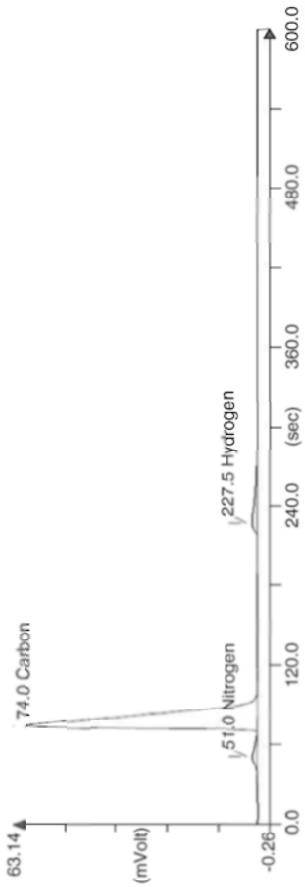

Fig. 2.5 CHN analysis for biochar sample

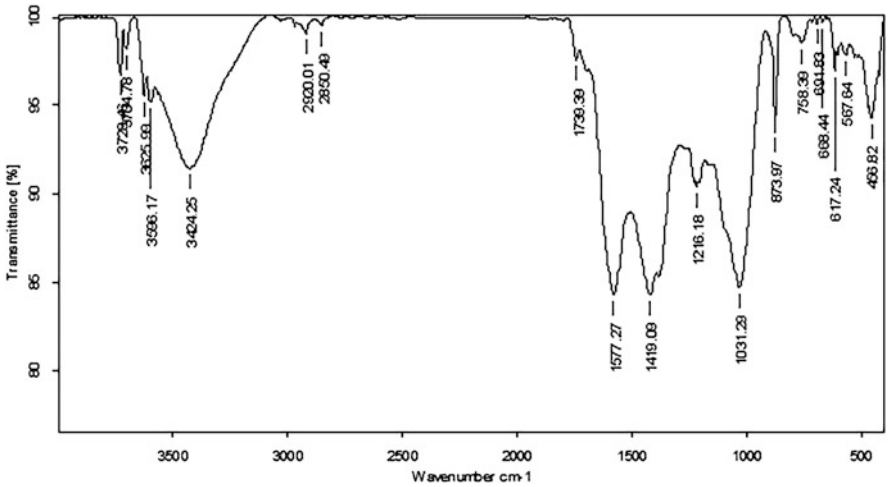

Fig. 2.6 FTIR spectroscopic image for biochar sample

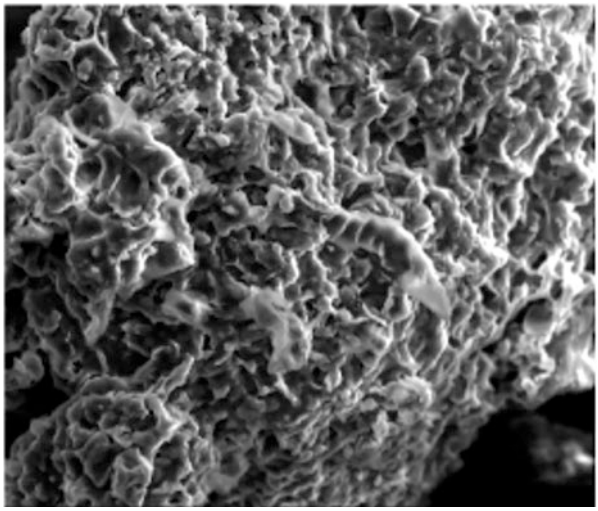

Fig. 2.7 SEM image of mustard biochar (Lucaci et al. 2019)

CaO and MgO. Hence, it can be concluded that biochar sample has a heterogeneous surface.

2.2.3.5 Physicochemical and Geotechnical Properties

The physicochemical properties of biochar as well as physicochemical and geotechnical properties of soil are represented in Table 2.1.

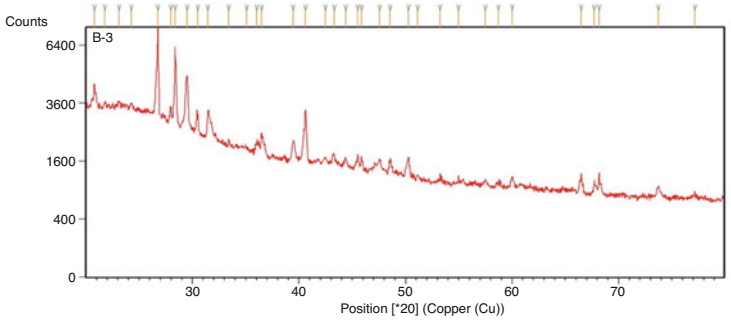

Fig. 2.8 XRD image for biochar sample

2.3 Effect of Biochar on Soil Properties

Reddy et al. (2015) studied the variation in the physicochemical and geotechnical properties of soil amended with varying proportions of biochar having different particle sizes. This study was found as the first of its kind in literature which considered geotechnical properties of the soil into account, and as per the results presented, soils amended with biochar were possessing improved geotechnical parameters to serve as stable landfill cover materials. Sadasivam and Reddy (2015) evaluated engineering properties of soils like compressibility and shear strength amended with biochar by using different types of seven biochars derived from wood. It was found that soil porosity, water-holding capacity and organic matter increase, whereas specific gravity decreases when biochar amendment is done. The shear strength of the soil also increases significantly by adding the biochar. Overall, the results were found quite encouraging in improving the soil properties.

Ding et al. (2016) reviewed the potential of biochar to improve soil fertility. It was observed that large surface area and nutrient content are the main characteristics of biochar. The authors discussed the effect of type of feedstock, pyrolysis temperature, pH, rate of application and different soil types along with mechanism behind the adsorption of nutrients by biochar. It was concluded that the negative effects reported by some studies and research gaps as well as uncertainties should be verified through further relevant investigations, especially long-term experiments. Alghamdi et al. (2018) performed an experiment to assess the impact of biochar combined with bentonite and compost with different application rates on physical and chemical characteristics of sandy soil. It was found that biochar and bentonite resist biodegradation in the soil and stay there for an extended time, whereas compost overcomes the negative impacts of chemical properties of soil.

Rajagopal et al. (2018) analysed the forecast of biochar in climate change mitigation with respect to Indian agriculture. The authors opined that biochar technology is in an emerging phase in India and still requires a general adoption by the farmers to take advantage of carbon sequestration, GHG offset, improved soil health and enhanced crop yields. They insisted for improved methods of biochar

production because the costs involved in collecting and transporting the residues restrict the adaptation. The authors suggested that biochar technology has more potential for soil carbon sequestration over the conventional methods of residue management in reference to Indian agriculture.

Mohan et al. (2018) conducted an experimental study by using two biochars made from rice husk and corn stover and observed that water-holding and cation exchange capacities and organic carbon increased, while carbon dioxide emissions decreased. The soil fertility and crop growth were also observed. The authors suggested that the problem of agricultural biomass burning in India can be resolved if it is pyrolysed to get biochar, and when biochar is applied to soils, it will not only improve soil properties but will also act as a carbon sink. However, they also insisted on large field trials for prolonged time to ensure the long-term benefits.

The biochar application to soil improves the physiochemical characteristics of soil due to its richness in organic carbon that makes the soil more fertile and acts as a carbon sequester. Biochar decreases the denitrification potential and lowers N_2O emission, greatly controlling leaching of mobile nutrients such as potassium and hence improving water use efficiency, nutrient availability and plant growth (Panwar et al. 2019).

A number of experiments and laboratory tests indicate that there are positive effects of adding biochar on the physicochemical and engineering properties of the soil. The initial parameters of virgin soil without mixing biochar were determined, and then different proportions by weight (% w/w) of biochar like 5%, 10%, 15%, 20% and 25% in dry condition were added to the soil sample, and the soil-biochar mix was thoroughly mixed. Various parameters of virgin soil and that of the soil amended with biochar are represented in Table 2.2 (Choudhary et al. 2022).

The results indicate that mixing of biochar to soil increases the organic carbon, organic matter, moisture content and water-holding capacity and at the same time decreases the specific gravity and density of the soil. The mechanism responsible for this improvement is the formation of macroaggregates in due course of time resulting in enhanced interparticle cohesion and improved resistance to slaking.

The consistency limits of soil-biochar mix have changed upon addition of biochar to it. The liquid limit of the soil increased from 43.12 to 48.75% (13.06% higher) upon addition of biochar at the rate of 25%. The increase in liquid limit is due to high porosity and large surface area of the biochar. The plastic limit of the soil also increased from 24.25 to 28.65% (18.14% higher) which can be attributed to greater water-holding and water-absorbing abilities of biochar. Similarly, the rise in shrinkage limit is seen from 17.63 to 21.85% (23.94% higher) which indicates towards higher void ratio in biochar as compared to the soil, and hence more water is required to change from solid state to semisolid state.

The Proctor test was used to learn about the compaction characteristics of soil-biochar. The value of maximum dry density (MDD) of the soil, i.e. 1.64 g cm^{-3}, decreased to 1.42 g cm^{-3} as the biochar was added to it. The probable reasons for reduction in MDD are the low specific gravity of biochar as compared to the soil. The value of optimum moisture content (OMC), i.e. 16.00%, increased up to 17.32% on addition of biochar which indicates that biochar has absorbed moisture from the

Table 2.2 Physicochemical and engineering properties of soil amended with biochar

S. No.	Characteristics	Values for soil amended with biochar (BC)						
		Virgin soil	Soil +5% BC	Soil +10% BC	Soil +15% BC	Soil +20% BC	Soil +25% BC	% *Variation*
1	pH	7.62	7.67	7.69	7.73	7.72	7.80	*2.36*
2	Specific gravity	2.56	2.54	2.53	2.52	2.52	2.51	*−1.95*
3	Moisture content (%)	11.12	11.48	11.85	12.38	12.82	13.22	*18.88*
4	Electrical conductivity (mS cm^{-1})	4.23	3.97	4.15	4.32	4.39	4.42	*4.49*
5	Organic carbon (%)	0.56	0.57	0.62	0.69	0.72	0.72	*28.57*
6	Organic matter (%)	0.98	1.01	1.04	1.06	1.07	1.07	*9.18*
7	Water-holding capacity (%)	32	36	38	40	42	44	*37.50*
8	Liquid limit	43.12	44.42	45.26	46.74	48.34	48.75	*13.06*
9	Plastic limit	24.25	25.43	26.12	27.28	28.45	28.65	*18.14*
10	Shrinkage limit	17.63	18.65	19.27	20.12	21.47	21.85	*23.94*
11	Plasticity index	18.87	18.99	19.14	19.46	19.89	20.10	*6.52*
12	Optimum moisture content (%)	16.00	16.42	16.93	17.12	17.24	17.32	*8.25*
13	Maximum dry density (g cm^{-3})	1.64	1.58	1.48	1.45	1.43	1.42	*−13.41*
14	Unconfined compressive strength (kg cm^{-2})	1.68	1.74	1.79	1.82	1.86	1.94	*15.48*
15	California bearing ratio (%)	1.96	2.06	2.12	2.17	2.22	2.31	*17.86*
16	Free swell index (%)	39	38	36	32	28	27	*−30.77*

soil. The value of California bearing ratio (CBR) increased from 1.96 to 2.31% (17.86% higher) upon addition of biochar to the soil sample. The increasing values of CBR show that addition of biochar to soil has affirmative effect on the bearing capacity of the soil and demonstrates to be an apt amendment for the soil (Choudhary et al. 2022).

Overall, it is observed that for the soil-biochar mix, the organic carbon increased by 28.57%, moisture content by 18.88%, water-holding capacity by 37.50%, unconfined compressive strength by 15.48% and CBR value by 17.86% and free swell index decreased by 30.77% on addition of biochar. Biochar is a marketable bioproduct which can be used in agriculture, industries and energy sector. Biochar can be transported easily, and it is cost-effective as compared to fertilizer. Also, it lasts longer on application to soil (Oni et al. 2019).

2.4 Effect of Biochar on Crop Yield

Nguyen et al. (2015) selected wheat and corn crops to study the effects of different ways to return biomass on soil and crop yield by taking two materials, one as the wheat and corn straw and another one as biochar made from them. The results demonstrated that biochar was capable of significantly improving the cation exchange capacity and organic matter in the soils. The direct application of straws showed poor results and had no contribution in increasing the crop yields. However, it promoted the plants to absorb nutrients. The application of biochar alone showed better results than that of the straws alone. Shareef and Zhao (2017) overviewed the basics of biochar as a tool for soil improvement and provided guidelines for the farmers and gardeners about biochar, its use and benefits so as to ensure enhanced yield and quality of crops. The authors anticipated that biochar improves the physical and chemical properties by way of raising water-holding capacity of soil and absorbing nutrients to decrease leakage and augmenting the soil structure due to large surface area and porosity of biochar. They concluded that fertility of soil and crop yields can be improved if proper application rate of biochar is maintained.

To study the effect of biochar application on yield of crops, three crops of bajra (pearl millet), wheat and mustard were chosen, and biochar was applied into the fields at different rates of 10, 20 and 30 t/ha for three consecutive seasons. It was observed that the yields of crop increase on addition to biochar into the fields. Table 2.3 shows the variation in crop yields.

It can be seen that the yields of bajra, wheat and mustard increase in all the three seasons in the range of 10.34–16.39%, and the maximum yield has been observed during the second season. When biochar is applied for the first time into fields, it takes some time to get adapted to soils and then absorbs micronutrients, holds water and other soil microbes in its pores and releases them when required by the plants during their growth. Hence, the maximum effect is observed during the second season, and, as time passes, some of the biochar gets flooded with water, and their

Table 2.3 Crop production during different seasons

S. No.	Name of crop	Crop production during	Crop produced (in q/ha) at the rate of application of biochar				*% Increase in yield*
			Without biochar	10 t/ha	20 t/ha	30 t/ha	
1	Bajra	First season	18.5	19.4	20.5	20.9	*12.97*
		Second season	18.3	19.2	20.6	21.3	*16.39*
		Third season	18.0	18.8	19.9	20.4	*13.33*
2	Wheat	First season	18.0	18.6	19.5	20.3	*12.78*
		Second season	17.8	18.6	19.7	20.5	*15.17*
		Third season	18.2	19	19.8	20.4	*12.09*
3	Mustard	First season	20.0	20.8	21.7	22.4	*12.00*
		Second season	19.7	20.6	21.9	22.8	*15.74*
		Third season	20.3	20.9	21.8	22.4	*10.34*

storage of nutrients and water starts diminishing, whose effect can be seen during the third season. Therefore, it is suggested to apply biochar into the fields after every 2 years so as to maintain the sufficient quantity of biochar in soils.

Rani et al. (2018) reviewed biochar as a boon for agriculture. According to them, the use of biochar for soil and agricultural improvement is an age-old known fact as per the benefits identified in the existing literature. There are environmental advantages also, but there are still some grey areas which need clarity like application rate, effects of feedstock and soil types and conditions. The authors suggested long-term field studies so as to optimize biochar application to ensure crop yields and a common recognition by the farmers. Biochar has numerous advantages and can be used in reducing the tensile strength of the soil, increasing pH and soil structure and increasing the efficiency of fertilizer use (Sun et al. 2012).

2.5 Conclusions

This paper provides a review of the available production methods of biochar and its further application to soils for improving the physicochemical and geotechnical properties. It can be concluded that biochar can be produced economically and efficiently at the fields by adopting the novel method of *BioCharan.* The agricultural waste and other crop residues can be utilized for producing biochar. Further application of biochar in soils has shown several environmental and economic paybacks. Soil properties have shown positive results upon addition of biochar in different proportions. The important geotechnical properties of soils including Atterberg's limits, MDD, OMC, swelling characteristics, unconfined compressive strength and CBR value have improved on addition of the biochar. Therefore, biochar application shows a promising potential for resolving the recurring nuisance of high air pollution in northern India, especially in the Indian capital city New Delhi due to crop residue burning in the nearby states. And, finally, *BioCharan* method can be called a multi-benefit method wherein the problem of crop residue burning is resolved by converting it to produce biochar, improvement in soil properties and increase in crop production can be ensured by way of applying biochar to soils and most importantly the environmental air pollution is minimized because there is no crop residue burning. Hence, the only thing required is to create awareness about this method among the stakeholders and encourage them to adopt it.

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Part II
Processes for Value Addition to Agricultural Waste

Chapter 3
Value-Added Products from Agricultural Wastes: Pectins from Cocoa Husk, Coffee Pulp, Soybean Hulls and Grape Pomace

C. Colodel, L. H. Reichembach, and C. L. O. Petkowicz

Abstract The agricultural, agroindustry and food industry generate huge amounts of plant wastes that are underutilized. Plant wastes consist mainly of cell wall. Depending on the type of material, cell wall from dicots can contain high amounts of pectin. Pectins are polysaccharides used as food additive. This chapter discusses the potential of cocoa pod husk, coffee pulp, soybean hull and grape pomace to be used as new raw material for pectin extraction.

Keywords Agricultural wastes · Cell wall · Pectin · Polysaccharide

3.1 Introduction

From the 1950s onwards, the world population has grown significantly, currently reaching around eight billion people (Worldometers, 8 Oct 2021). Meeting the food and nonfood needs of this large number of people requires extensive agricultural production and manufacturing activity. Agricultural crop and agro-industrial activities generate a large amount of plant waste, whose management represents a great challenge. These wastes are often discarded in landfills or other disposal sites or left to rot on the land to act as fertilizer. However, they can change the pH of the environment, modify the soil microbiota and spread diseases. The fact that many crops are concentrated in harvest seasons aggravates this problem due to the accumulation of huge amounts of waste (Ravindran and Jaiswal 2016).

About 1.3 billion tonnes of food wastes is produced annually around the world, and approximately 60% is made up of plant-based materials (Sagar et al. 2018). In addition, nonfood crops, such as cotton, jute, castor seed and tobacco, also generate massive amounts of plant waste (Patel 2017; Herculano et al. 2016; Nayak et al.

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2013). All these wastes are mainly composed of cell wall, the highly complex structure that surrounds the plant cells. Two main types of cell wall can be identified in terrestrial plants, primary cell wall and secondary cell wall. Irrespective to the type, plant cell walls are mainly composed of polysaccharides, namely, cellulose, hemicelluloses and pectins. Primary cell walls are found in every plant cell and contain high amounts of pectin. However, secondary walls are deposited only in certain specialized cells and are distinguished from primary walls by the presence of lignin, low levels of pectin and higher amounts of cellulose (Caffall and Mohnen 2009). Many studies have addressed the use of this lignocellulosic biomass for production of biofuels and chemicals (Carpita and McCann 2020). On the other hand, plant wastes containing mainly primary cell wall can be used as raw material to extract pectin, a hydrocolloid commercially available, which has several uses, mainly in the food industry. This chapter focuses on the possibility of using abundant wastes from processing of commodities for pectin production. Initially, a brief explanation about plant cell wall and pectins is provided. Then, the availability, composition and advances in the usage of cocoa husk, coffee pulp, soybean hulls and grape pomace and their potential as feedstock for pectin extraction are discussed. Just for clarity, each plant waste is discussed in a different section.

3.2 Plant Cell Wall

The plant cell wall is a complex and organized structure composed of different polysaccharides, proteins and/or phenolic compounds (Holland et al. 2020). It is deposited in the plant cell as layers, which are established in distinct stages of development. The middle lamella, the adhesive material between adjacent cells, is the first layer formed, followed by the primary wall. They are deposited in the cell division, and as the cell enlarge, the primary wall increases in surface area. When the cell growth stops, at differentiation, many cells deposit a secondary cell wall, which is usually strengthened by the presence of lignin, a complex hydrophobic phenolic polymer. Lignocellulosic biomass consists of plant material containing secondary wall. On the other hand, edible plant tissues and soft parts of plant contain predominantly primary wall.

Polysaccharides can account for 90% of the dry weight of primary cell wall and 10% of secondary wall. The relative amount and type of polysaccharides varies between primary and secondary walls as well as with the plant taxa. Cellulose is the best-known cell wall polysaccharide. In the cell wall, cellulose microfibrils are associated by hydrogen bonds to polysaccharides named hemicelluloses. The main hemicelluloses are xyloglucans and glucuronoarabinoxylans in primary walls and xylans and (galacto)glucomannans in secondary walls, but others can occur in minor amounts. The third type of cell wall polysaccharides is the pectins. They are particularly abundant in the primary cell wall of dicots and noncommelinoid monocots (up to 35%) and the middle lamella, while it is found in low amounts in

commelinoids (2–10%) and secondary walls (up to 5%) (Caffall and Mohnen 2009; Mohnen 2008).

3.3 Pectin

The term pectin describes a group of heterogeneous polysaccharides that contain galacturonic acid (GalA), which include the homogalacturonan (HG), rhamnogalacturonan I (RG-I), rhamnogalacturonan II (RG-II) and xylogalacturonan. Most of the pectin in the plant cell wall is HG, followed by RG-I. Together, they account for around 80–95% of pectins (Caffall and Mohnen 2009; Mohnen 2008).

HG consists of linear chains of GalA. In these chains, the carboxyl groups from GalA units can be either negatively charged or ionically associated with calcium ions or methyl-esterified (Fig. 3.1). The proportion of GalA units that is methyl-esterified defines the degree of methyl esterification (DM). Pectins with DM $\geq$ 50% are categorized as high-methoxyl (HM), while those with DM $<$ 50% are low-methoxyl (LM). Acetylation can also occur at O-2 and/or O-3. In the RG-I, alternate units of GalA and rhamnose form a backbone to which side chains of arabinans, galactans and/or arabinogalactans are attached (Mohnen 2008).

Pectins can be removed from cell wall by extraction with water, chelating agents, diluted alkali or diluted acid, often with heating. The composition and properties of the pectin are highly dependent on the extraction conditions. Usually, dried plant material is used, and some treatment can be made prior to extraction to remove pigments and free sugars among other low molar mass compounds. Academic researchers usually perform a pretreatment with ethanol resulting in an alcohol insoluble residue (AIR) which is further extracted to isolate the pectin. Pectins from citrus peel and apple pomace (remaining after juice and cider production) are commercially available. In the industry, pectins are obtained by extraction with

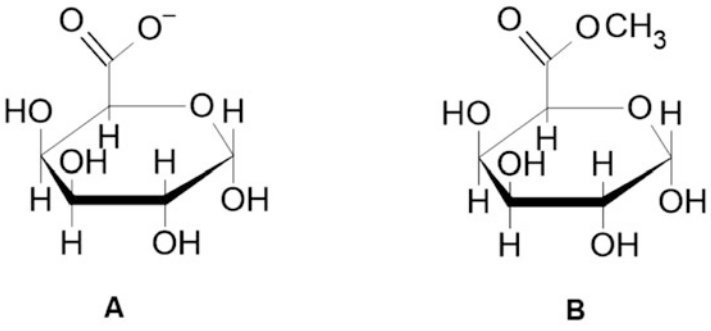

Fig. 3.1 Chemical structure of galacturonic acid (GalA) negatively charged (**a**) and methyl-esterified (**b**)

mineral acid at pH values 1.0–3.0, for 1–12 h at 50–100 °C. The proportion of raw material and solvent, the solid/liquid ratio (w/v), is also an important parameter that affects extraction yield. The extract containing pectin is separated from the solid residue by filtration. Then, the pectin is isolated from the liquid phase by precipitation with alcohol (usually isopropanol or ethanol) followed by filtration and drying (Rolin 1993). The hot acid extraction of pectin used by industry has been called 'conventional extraction' to differentiate from new approaches that have been used in research studies such as extraction assisted by microwave, ultrasound, enzymes and ultrahigh pressure, among others (Das and Arora 2021; Kumar et al. 2020).

The pectin is mainly used as food additive due to the thickening, stabilizing and gelling properties. It is used in jams, jellies, fruit beverages, desserts, bakery and dairy products. Most of regulatory food agencies require a minimum of 65% galacturonic acid calculated on the ash-free and dried basis. Gelation occurs under specific conditions that depends on the pectin DM. LM pectins form gel by interaction with calcium ions and HM pectin gel in acidic media (usually pH < 3.5) in the presence of high sugar concentration (generally 60–65% sucrose). However, pectins with low molar mass or high amount of acetyl cannot form gel (Reichembach and Petkowicz 2021). Typically, pectins with more than 4% acetyl do not gel (Iglesias and Lozano 2004), such as the pectin from sugar beet pulp. Other structural features, as the distribution of the methyl ester groups and the pectin side chains, also affect the gelation.

Apart from the traditional uses as food additive, other applications have been proposed for pectins, such as emulsifiers, for edible films and modified pectin commercialized as dietary supplement to promote health and longevity (Nastasi et al. 2022; Alba and Kontogiorgos 2017). New uses increase the demand for pectin justifying the search for alternative raw materials. In addition, the use of only two plant materials for pectin extraction can limit the production in the poor crops resulting in shortage of pectin (Reichembach and Petkowicz 2021). Plant wastes from dicots, such as cocoa pod husk, coffee pulp, soybean hulls and grape pomace, available in high amounts are potential candidates to be used for pectin extraction.

3.4 Cocoa Pod Husk

Chocolate is one of the most consumed and appreciated sweets around the world. The raw material from which chocolate and its related products are produced is cocoa (*Theobroma cacao*) beans. Europeans are the largest consumers of cocoa beans (45% of production), followed by Americans (32%, mainly in the USA) (Swiss Platform for Sustainable Cocoa, 10 Oct 2021). The production of cocoa-based products is concentrated in Europe and the USA, but the African continent is responsible for 76.1% of all raw materials for chocolate production (STATISTA, 10 Oct 2021b). Ironically and sadly, due to the lower incomes in the region, the African continent has the lowest consumption of sweet products from cocoa beans, consuming only 4% (Swiss Platform for Sustainable Cocoa, 10 Oct 2021).

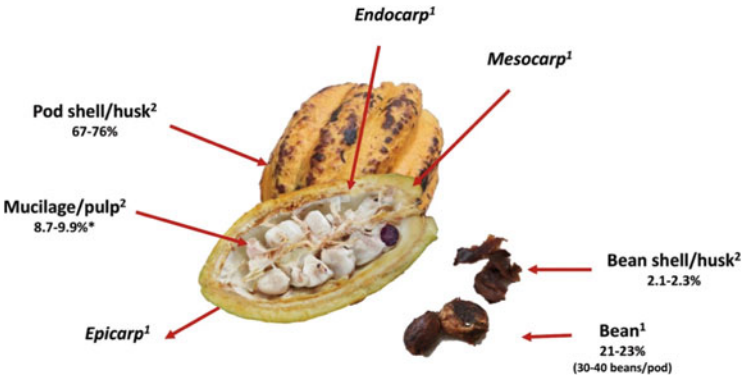

Fig. 3.2 Structures of the cacao fruit and its respective proportions on the weight of fruit. (Reprinted from Campos-Vega et al. 2018, with permission of Elsevier)

The cocoa fruit is composed of 21–23% beans, covered by a bean shell which corresponds to 2.1–2.3%, 8.7–9.9% pulp and 67–76% pod husk, as shown in Fig. 3.2 (Campos-Vega et al. 2018). Thus, cocoa pod husk accounts for most of the weight of the fruit.

For cocoa industry, only seeds are of commercial importance; they are removed, fermented and processed to generate commercial products, mainly chocolate and cocoa butter, as shown in Fig. 3.3. The husks are therefore completely discarded after the seeds are removed, becoming the main waste of the cocoa industry (Campos-Vega et al. 2018). For every tonne of cocoa beans produced, about 10 tonnes of pod husk waste is generated (Figueroa et al. 2020).

3.4.1 Composition and Uses of Cacao Pod Husk

The most common use of cocoa pod husks is the discard in the farm as an organic fertilizer. Nevertheless, this practice has a drawback as the material may often be contaminated with plant disease-causing species, particularly *Phytophthora* spp., which cause a disease known as black pod rot. Black pod rot causes annual losses of 20–30% in world cocoa production, while some cocoa producers may have annual losses of up to 90% (Lu et al. 2018). However, the chemical composition of the cocoa husk (Table 3.1) suggests other possibilities for the use of this residue.

Due to the high potassium content (Table 3.1), cacao pod husk has been used to obtain potassium hydroxide for soap making (Lu et al. 2018). Other low-value applications include activation to produce activated carbon and animal feed (Lu et al. 2018). The use of cacao pod husk in animal feed has been evaluated for different species. The replacement of conventional ingredients used in the manufacture of feed by cacao pod husk reduces the costs and appears to not cause significant changes in the nutrition of fish (Pouomogne et al. 1997), rabbit (Ridzwan et al. 1993)

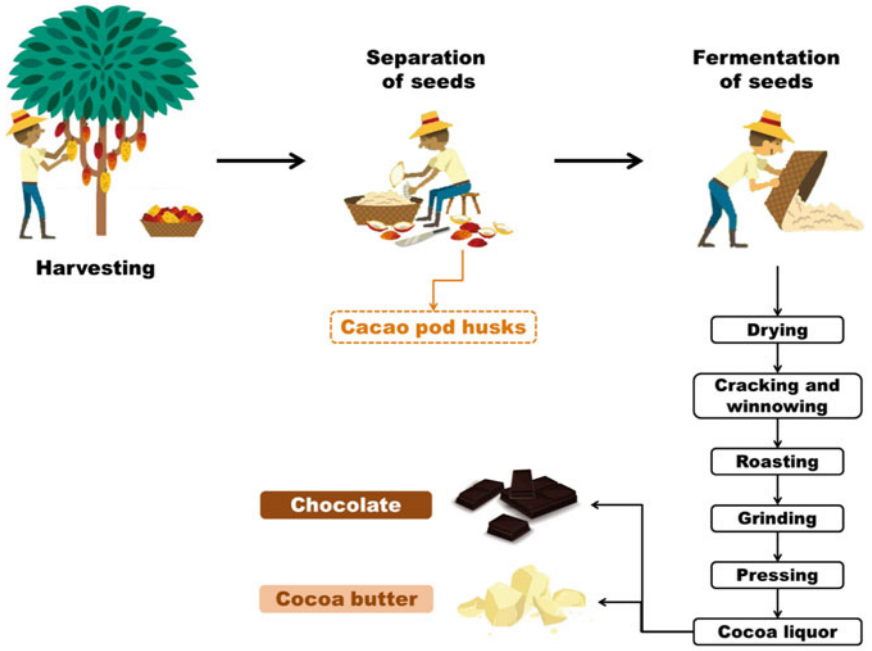

Fig. 3.3 Steps of cocoa processing. (Adapted by the authors from https://www.hechosconcorazon.com)

and pig (Oddoye et al. 2010). However, fishes that were fed diets containing cacao pod husks had a reduction in carcass protein content (Pouomogne et al. 1997), and rabbits showed a slight decrease in energy digestibility (Ridzwan et al. 1993). When used as an ingredient in broiler chick feed, cocoa pod husk led to adverse effects such as a 60% increase in feed intake, increased water intake and decreased animal growth (Donkoh et al. 1991). The negative effects observed in animals fed with a diet supplemented with cacao pod husk were attributed to the low digestibility of the material due to the high content of crude fibres. For this reason, several studies have been carried out seeking previous treatments that improve the bioavailability of the nutrients present in the cocoa husk that allow a better digestive use of this material in animal feed (Campos-Vega et al. 2018). Nevertheless, pretreatments result in increased costs, which may result in unprofitable cost/benefits for the use of cocoa husks in animal feed.

On the other hand, the composition of cacao pod husk (Table 3.1) favours its use for higher value applications. Among the proteins present in cacao pod husks, enzymes that are extensively used in various industrial processes can be isolated, such as hydrolases (Yusof et al. 2016) and lipases (Khanahmadi et al. 2015, 2016). It can also be used for production of bioethanol (Hernández-Mendoza et al. 2021; Valladares-Diestra et al. 2022a) and propionic acid (Sarmiento-Vásquez et al. 2021) by fermentation of the hydrolysed material.

Table 3.1 Chemical composition of cocoa pod husk

Component[a]	Mass fraction (%)[b]
Moisture	80.2–90
Protein	7–10
Lipids	0.6–4.7
Ash	6.7–15
Dietary fibre	18.3–59.0
Cellulose	19.7–35.4
Hemicellulose	8.7–37.0
Pectin	6.1–33.46
Lignin	6.0–30.18
Total phenolics	0.46–0.69[c]
Mineral contents	
Ca	0.25–0.46
K	2.8–3.8
P	0.19–0.4
Mg	0.11–0.25
Mn	0.036–0.05
Na	0.01–0.5
Cu	0.0006–0.003
Fe	0.003–0.006
Zn	0.004–0.006

[a] From Vriesmann et al. (2011a), Campos-Vega et al. (2018), Lu et al. (2018) and Vandenberghe et al. (2022)
[b] Based on the dry weight of cocoa pod husk, except for moisture
[c] Expressed as % of gallic acid equivalents

Dietary fibres present in cocoa husks have good swelling and water-holding capacity and can delay glucose absorption (Lecumberri et al. 2007). Cocoa pod husk flour can be used as an ingredient in the formulation of sausages (Delgado-Ospina et al. 2021), breads (Amir et al. 2013) and snacks (Jozinovic et al. 2018), increasing the dietary fibre content in these foods and improving their sensory properties.

3.4.2 Potential of Cocoa Pod Husk as Source of Pectins

The investigation on cacao pod husk pectins began in the middle of the twentieth century, with studies of Dittmar (1958). Using hot water extraction, the author recovered a fraction containing pectin and other polysaccharides from sun-dried pod husk from South American varieties of cocoa. Later, the cell wall polysaccharides from cacao pod husks were fractionated by sequential extractions, and pectic polysaccharides were identified as the major polymers (Blakemore et al. 1966). Over the years, more studies were carried out focusing on cocoa pod husk pectins, and the methodologies used and the results obtained are summarized in Table 3.2.

Table 3.2 Yield and chemical features of pectins extracted from cocoa pod husks under different conditions

Harvest region	Extracted material	Extraction conditions	Yield (%)	GalA (%)	DM (%)	DA (%)	References
South America	Sun-dried pod husk	Hot H_2O	11	n.d.	n.d.	n.d.	Dittmar (1958)
Ghana	AIR from sun-dried milled husk	Sequential extraction: H_2O, 100 °C, 3 h; 0.5% ammonium oxalate, 100 °C, 2 h; 10% KOH, 20 °C, 2 h; 20% NaOH, 75–85 °C, 5 h	11	27	n.d	n.d.	Blakemore et al. (1966)
			8	–			
			10	–			
			12	–			
Ghana	Dry ripe and unripe chopped pod husk	Boiling 0.2 N acetic acid, pH 2.8, 20 min; 0.05–0.1 N HCl, pH 2.8, 80 °C, 20 min	25–29 (unripe)	62 (unripe)	n.d.	n.d.	Adomako (1972)
			8–11 (ripe)	62 (ripe)			
Ghana, Ecuador and Ivory Coast	Dry milled defatted hulls	Sequential extraction: H_2O, 1:30 w/v, 75 °C, 15 min; 0.75% HMP, pH 3.5, 75 °C, 60 min	n.d.	44–47 (water)	61 (HMP)	n.d.	Arlorio et al. (2001)
				11 (HMP)			
Venezuela	Dry milled pod husks	0.5% EDTA, 1: 26.7 w/v, 60 min	4	62	48	n.d.	Barazarte et al. (2008)
		Factorial design 3^2 varying pH (3–5) and temperature (60–90 °C)					
		Optimized conditions: pH 4, 90 °C					
Ghana and Venezuela	Whole or minced dry milled pod husks, microwave pretreated or not	H_2O, 1:25 w/v, pH 7 or pH 4, 2.5, 1.5 or 1 acidified with HCl, 95 °C, 1, 2 or 3 h	n.d.	2–8	31–47	2–3	Mollea et al. (2008)
Brazil	Dry and milled pod husks	H_2O, 1:25 w/v, 50 and 100 °C, 90 min	8–13	45	37	29	Vriesmann et al. (2011a)
				45	43	19	
Brazil	Dry and milled pod husks	HNO_3, 1:25 w/v; fractional factorial design 3^{3-1} varying pH (1–3), temperature (50–100 °C) and time (30–90 min);	10	66	57	17	Vriesmann et al. (2011b)

(continued)

Table 3.2 (continued)

Harvest region	Extracted material	Extraction conditions	Yield (%)	GalA (%)	DM (%)	DA (%)	References
		central composite design varying pH (1.79–3.21) and temperature (70.86–99.14 °C)					
		Optimized conditions: pH 1.5, 100 °C, 30 min					
Brazil	Dry and milled pod husks	Citric acid, 1:25 w/v; fractional factorial design 3^{3-1} varying pH (1–3), temperature (50–100 °C) and time (30–90 min); central composite design varying pH (1.79–3.21) and temperature (70.86–99.14 °C)	10	65	40	16	Vriesmann et al. (2012)
		Optimized conditions: pH 3, 95 °C, 95 min					
Ivory Coast	Dry AIR from milled pod husks	HNO_3, 1:25 w/v, 75 °C 90 min, pH 1–3	5	75	37	3	Yapo and Koffi (2013)
			9	65	52	6	
			4	51	44	10	
India	Minced dry pod husks	Ascorbic acid, 1:10 w/v; fractional factorial design 3^{3-1} varying pH (1.5–3.5), temperature (90–100 °C) and time (30–60 min); central composite design varying pH (1.0–4.2), temperature (86.6–106.4 °C) and time (19.8–70.2 min)	4	74	8	n.d.	Priyangini et al. (2018)
		Optimized conditions: pH 2.5, 95 °C; 45 min					
Brazil	Dry milled pod husks	Citric acid, central composite design varying temperature (120–170 °C),	19	n.d.	52	n.d.	Valladares-Diestra et al. (2022b)

(continued)

Table 3.2 (continued)

Harvest region	Extracted material	Extraction conditions	Yield (%)	GalA (%)	DM (%)	DA (%)	References
		time (10–30 min) and acid concentration (0.5–2% w/v)					
		Optimized conditions: 2% w/v, 120 °C, 10 min					

GalA galacturonic acid, *DM* degree of methyl esterification, *DA* degree of acetylation, *n.d.* not determined, *AIR* alcohol insoluble residue, *HMP* sodium hexametaphosphate

As expected, the amount/availability of pectins depends on the ripening stage of cacao pod husk. When ripe and unripe (named cherelles) pod husks were extracted using acetic and hydrochloric acid at 80 °C, cherelles provided about three times higher yield of pectins compared to the ripe ones (Adomako 1972). The polysaccharides extracted with acetic acid, conditions similar to the method used for industrial production of pectins, from ripe and unripe pod husks had GalA content of 62%, close to the minimum required for commercial purposes.

After a gap of almost 30 years, in 2001, the composition of cacao pod husk and its potential as an alternative source of pectins was investigated (Arlorio et al. 2001). Antinutritional compounds, like phytic acid and trypsin inhibitors as well as potentially toxic biogenic amines, were identified. However, the presence of these compounds does not limit the use of the husks as pectin source since treatment with 2-propanol may be used to remove them prior to the pectin extraction. The pod husks were firstly submitted to water washing and subsequentially to pectin extraction with sodium hexametaphosphate solution. The pectin was precipitated from the extract by adding a 1/5 volume of 1 M HNO_3, different from the technique used in the industrial production of pectin, which uses alcohols as precipitating agents. This procedure resulted in precipitation of a pectin gel, which was recovered and had a DM of 60%. Analyses of GalA content showed that a large part of pectin was dissolved in the prior water washing.

Further studies using a chelating agent were performed by Barazarte et al. (2008) using 0.5% EDTA as extractant at solid/liquid ratio of 1:26.7 for 60 min. A 3^2 factorial design was used to evaluate the effect of pH (3–5) and temperature (60–90 °C) in the extraction of pectins from cacao pod husk. LM and HM pectins were obtained. Interaction between pH and temperature in the extraction process of pectins from cacao pod husk was observed, and the best conditions for pectin recovery, among the tested conditions, were found to be pH 4 at 90 °C. These conditions resulted in 4% yield and GalA content of 62%, similar to the values found by Adomako (1972) using acetic acid as solvent. In this study, the gelling properties of pectins from cacao pod husk were investigated for the first time, but not all showed gelling capacity under the conditions tested. Only the pectins with higher

DM and molar mass were able to form gels at concentration of 0.5% in acidic medium and presence of Ca^{2+} (30 mg/g of pectin) and 30% of soluble solids.

Conditions similar to those used for pectin industrial production, were used by Mollea et al. (2008). Cacao husks from Ghana (whole or minced) and from Venezuela (minced) were used and the effect of microwave pretreatment, extraction time (1, 2 or 3 h) and pH (HCl, 1.0–7.0) on the yield and GalA content of pecins was evaluated. The origin of the plant material showed to be not statistically significant, as well as the microwave pretreatment. Mincing the husks previously enhance de contact area between the plant material and the extractant and as expected, improve the pectin recovery compared to the whole material. At pH 7, higher times resulted in higher pectin yields, but time did not have a significant effect at lower pH values (1.0–2.0), at which higher amounts of pectin were obtained. Only LM pectins were obtained, and the lower the pH, the lower the DM. Similar effect of pH was observed on the degree of acetylation of pectins, which decreased with the decrease in the pH.

In the last decade, Vriesmann et al. (Vriesmann et al. 2011a,b, 2012; Vriesmann and Petkowicz 2013, 2017) published a series of studies on the extraction of pectins from cacao pod husks. Using extractions with water at 50 °C and 100 °C (solid/liquid ratio 1:25, 90 min), these authors isolated pectic polysaccharides with yields of 7.5% and 12.6%, respectively (Vriesmann et al. 2011a). The polysaccharides had ~45% of GalA and high levels of galactose and rhamnose, indicating highly branched structures, low degree of methoxylation and high degree of acetylation. High degrees of acetylation were also found in the pectin extracted with nitric acid, pH 1.5, at 100 °C for 30 min (Vriesmann et al. 2011b). This condition was determined using the response surface methodology which evaluates the effect of pH, temperature and time on the yield and uronic acid content of pectins. The pectin extracted in the optimal conditions had 9.0% yield, DA 17%, DM 57% and 66.0% GalA. It was the first time that a study reported a GalA content above 65%, thus meeting the commercial criteria for pectins. Despite the high DA, which is known to hinder the formation of gel, the optimized pectin from cacao pod husk was able to form gel by the usual way for HM pectins. The best gel properties were achieved at a concentration of 1.32% GalA, 60% of sucrose at pH 2.7 (Vriesmann and Petkowicz 2013).

Nitric acid at different pH (1.0–3.0) was also used by Yapo and Koffi (2013) as solvent for pectin extraction from cacao pod husk. Although the highest GalA content (75%) was found in the pectin extracted at pH 1.0, the pectin extracted at pH 2.0 had the highest yield (9%), DM (52%) and average molar mass with 65% GalA. It was the only one able to form gel in acidic medium containing 55–75% sucrose. The DA of pectins ranged from 3 to 10%, increasing as the pH increased. The DA of 6% did not prevent the gel formation of the pectin, in agreement with the results reported by Vriesmann and Petkowicz (2013) for acetylated pectins from cacao pod husk.

The optimization of pectin extraction from cacao pod husk using citric acid resulted in 10% yield of a LM pectin composed of 65% GalA and DA of 16%. Although the citric acid-optimized pectin was LM with high DA, it forms a weak gel at concentration of 0.99% GalA, 60% sucrose at pH 2.7–3.0 (Vriesmann et al. 2012).

Although the citric acid-optimized pectin was LM with high DA, it forms a weak gel at concentration of 0.99% GalA, 60% sucrose at pH 2.7–3.0. Later, Vriesmann and Petkowicz (2017) demonstrated that the water-soluble pectin extracted at 100 °C (Vriesmann et al. 2011a) and the nitric acid-extracted pectin at 30 min, pH 3.5 and 100 °C, both LM (DM 43% and 41%, respectively) and containing high amounts of acetyl (DA 19% and 18%), were also able to form gels in acidic medium with high sucrose content, suggesting the potential application of pectins from cacao pod husk as gelling agents.

The search for improving the process of extracting pectins from the cocoa pod husk continues, and, more recently, some studies have obtained excellent results. Applying response surface methodology, Priyangini et al. (2018) optimized ascorbic acid-mediated extraction of pectins from cacao pod husk using a full factorial design followed by central composite design to determine the optimal pH, time and temperature to improve the yield and the uronic acid content of pectins. The yield of pectins extracted ranged between 2 and 5.2%, below the yields obtained previously (Adomako 1972; Vriesmann et al. 2011a, b, 2012; Vriesmann and Petkowicz 2017; Yapo and Koffi 2013), but the uronic acid content was much higher than that found in any previous publication, ranging from 49.4 to 90%. Aiming the best yield and uronic acid content simultaneously, the best extraction condition was pH 2.5 at 95 °C for 45 min, resulting in yield of 4.2% and uronic acid content of 74.5%. One more time, a low methyl-esterified pectin was obtained, with DM of 8.1%.

Recently, Valladares-Diestra et al. (2022b) used hydrothermal pretreatment assisted by citric acid for extraction of pectin and xylooligosaccharide production from cacao pod husk. A central composite design was employed to optimize the extract conditions, varying the temperature (120–170 °C), time (10–30 min) and citric acid concentration (0.5–2% w/v). The pectin yields (0.7–20%) were greatly improved by this process compared to the previous studies. However, since GalA was not quantified, the quality of the pectin extracted is not assured.

Studies published so far on pectins from cocoa pod husks show that cocoa is a potential source of pectins, particularly with a low degree of methyl esterification. The extraction process has been improved over time, and conditions for extractions with good yield and GalA content that meet commercial requirements have already been established and continue to be investigated to improve the process. Even with the presence of acetyl in amounts greater than desirable for commercial pectins, it has already been demonstrated that cocoa pectin is able to form gels and could be used as thickening and gelling agents.

3.5 Coffee Pulp

Coffee is a widely appreciated beverage and valuable commodity. *Coffea arabica* and *Coffea canephora* (*Coffea robusta*), known as arabica and robusta, respectively, are the most important commercial species. They differ in the morphological features and composition of the beans (Portela et al. 2021). Robusta has higher

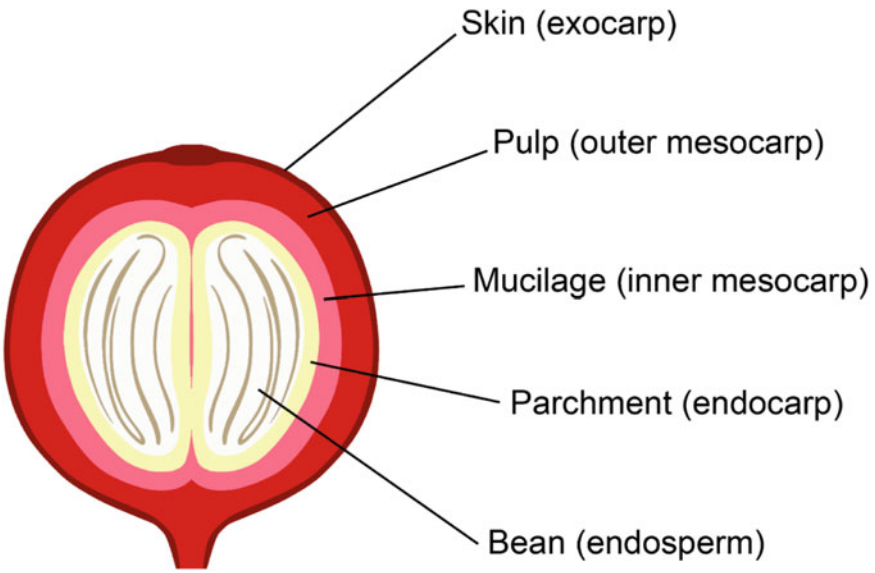

Fig. 3.4 Schematic representation of a longitudinal section of coffee cherry and its constituents. (Kindly designed by Deise G. Bariviera)

caffeine levels than arabica. In addition, robusta has higher crop yield, and it is more resistant to diseases. On the other hand, arabica stands out for its more enjoyable flavour (Chanakya and De Alwis 2004). The main producers are Brazil and Vietnam, accounting for ~65% of the world production, which was of 10.5 million tonnes of beans in 2020 (International Coffee Organization, 10 Nov 2021).

In the course of processing, wastes are produced, since the constituents involving the bean have to be removed in order to achieve the final product. One of these wastes is coffee pulp, the main solid residue from coffee wet processing. For every 2 tonnes of coffee cherries processed, nearly 1 tonne of pulp is generated (Roussos et al. 1995). The waste so-called coffee pulp consists of the skin (exocarp) and the pulp (outer mesocarp) of the fruit (Rodríguez-Durán et al. 2014), but a small amount of mucilage and parchment may also be found in the biomass. Figure 3.4 illustrates the different layers of coffee cherry.

3.5.1 Coffee Processing and Wastes

Coffee processing can be carried out by dry or wet methods (Fig. 3.5). The choice of method goes through some fundamental considerations, including the cost/benefit, the environmental legislation and the desired quality standard of the coffee. The dry process is predominant for *C. canephora* crops worldwide and *C. arabica* in Brazil,

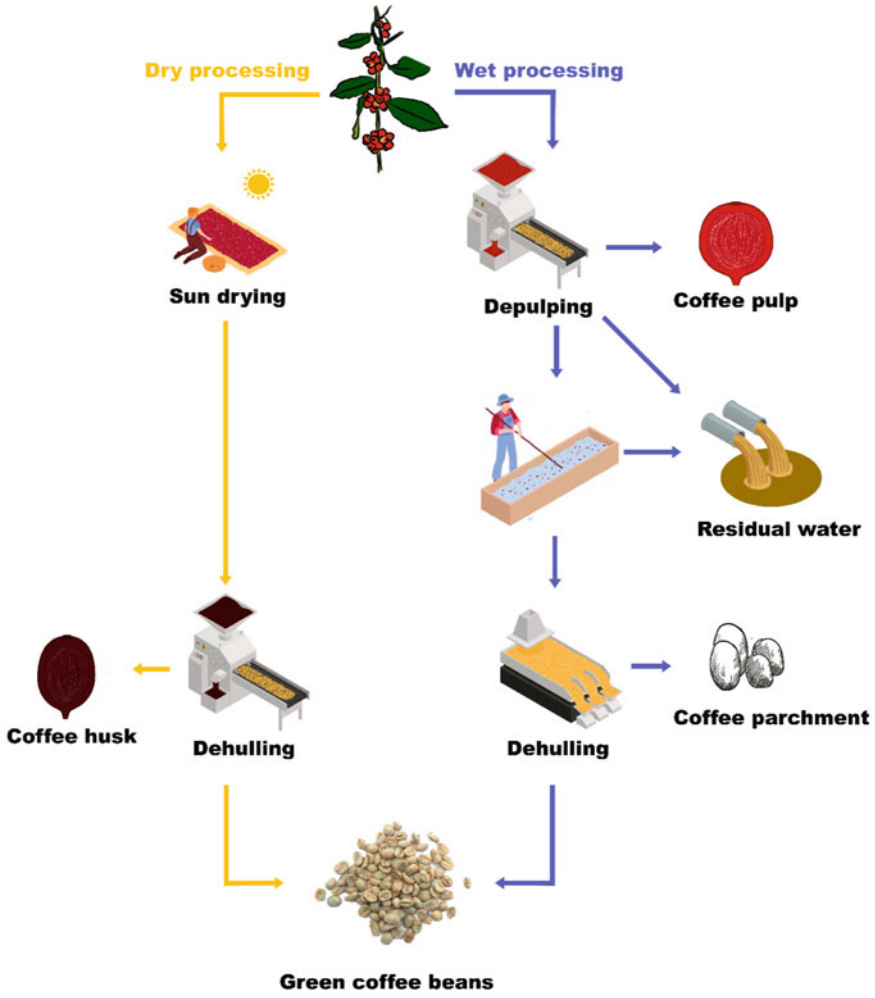

Fig. 3.5 Main steps of coffee processing (dry and wet) and produced wastes. (Adapted by the authors from Freepik and Pixabay, under free license)

while, for *C. arabica*, the wet process is preferred in most of the countries (Guimarães et al. 2019). In the dry processing, coffee cherries are spread in yards, in thin layers of 5–10 cm, and dried under the sun. After 3–4 weeks, when the moisture is below 12%, the fruits are dehulled, generating the waste known as coffee husk.

The wet process includes the removal of cherry pulp followed by a fermentation step. In general, it results in coffees with higher quality and economical value (Alves et al. 2017). This method requires processing equipment, high amount of clean water and the exclusive harvesting of ripe fruits. The crop is placed into a receiving tank

equipped with an overflow weir to remove the floaters (dry and insect-infested berries, leaves and sticks) (Vincent 1987). Then, the ripe berries are depulped by squeezing the fruit between two serrated metal plates, allowing the skin and pulp to be separated from the seeds. This is the step where a large amount of coffee pulp is produced (Chanakya and De Alwis 2004). The seeds, covered by mucilage, proceed to the fermentation step. The fermentation is most commonly carried out by enzymes that naturally occur in coffee and is critical for removing the mucilaginous layer from the parchment coffee. The presence of mucilage can prolong the drying process of coffee beans and lead to mould development (Haile and Kang 2019). Control of pH is essential to avoid the development of undesired microorganisms that promote the production of off-flavours and excess of organic acids, such as propionic acid. Fermentation often improves coffee quality by the degradation of some polyphenols and diterpenes, leading to a reduction of hardness and bitterness in the brew (Vincent 1987). After the removal of the mucilage, the beans are washed, dried and dehulled for removal of coffee parchment. Water in abundance is needed during these steps and can achieve 15 m^3 per tonne of fruits (Rattan et al. 2015). In the end of both processing methods, green coffee beans are obtained, along with the waste streams generated during processing.

3.5.2 Composition and Uses of Coffee Pulp

The chemical composition of coffee pulp is shown in Table 3.3. Differently from coffee husk, coffee pulp presents high levels of moisture. Most of its potential uses

Table 3.3 Chemical composition of coffee pulp

Component[a]	Mass fraction (%)[b]
Moisture	76.7–82.4
Protein	7.5–15
Lipids	2.0–7.0
Ash	8.3
Carbohydrates	21.0–50.0
Dietary fibre	28.0–61.0
Cellulose	43.0–63.0
Hemicellulose	2.3–3.6
Pectin	6.5–14.6
Lignin	17.5–22.0
Tannin	1.8–8.6
Caffeine	1.3–1.5
Chlorogenic acid	2.4–2.6
Caffeic acid	1.6

[a] From Bressani et al. (1972), Cañas et al. (2021), Elías (1979), Gurram et al. (2016), Murthy and Naidu (2012), Pandey et al. (2000), Reichembach and Petkowicz (2020) and Wilbaux (1956)
[b] Based on the dry weight of coffee pulp, except for moisture

would benefit from pressing the pulp to reduce moisture level to 55–60%. Previous studies suggested uses that include animal feed and fertilizer (Bressani 1979). The attempts in adding coffee pulp (and coffee husks) to animal feed formulations were only partially successful due to the limitation on the amount of material that could be used without compromising the quality of the livestock feed. On the other hand, coffee pulp can be a good option as fertilizer for potassium-depleted soils. Controlled composting produces biomass that can be used to increase water retention and improve long-term quality of the soil (Oliveira and Franca 2015). Other uses include biogas, alcohol, enzymes, organic acids and mushroom production (Corro et al. 2013; Pleissner et al. 2016; Salmones et al. 2005; Shenoy et al. 2011; Torres-Mancera et al. 2011; Velázquez-Cedeño et al. 2002). Nevertheless, coffee pulp remains mostly unused, primarily due to the presence of high amount of antinutritional factors, as caffeine, tannins and polyphenols, that diminishes the acceptance of food and absorption of nutrients. These compounds also confer toxicity to the pulp, impairing its consumption and contributing to environmental pollution. Different procedures (treatment with alkali, water, ensilaging, etc.) have been tested to decrease the levels of these compounds (Bressani 1979; Pandey et al. 2000). Some of the antinutrients, such as caffeine and chlorogenic acid, have commercial value and can be successfully extracted from coffee pulp. Caffeine content in the pulp of *C. arabica* seems to be higher than *C. canephora*, the reverse situation from the beans (Clifford and Ramirez-Martinez 1991; Loukri et al. 2020).

The amino acid profile of coffee pulp makes it an attractive protein source, especially for essential amino acids. Lysine, valine and leucine are essential amino acids found in high amounts in coffee pulp, while sulphur-containing amino acids are scarce. However, availability of protein is still a constraint, since molecules present in the coffee biomass, especially tannins, can bind protein, leading to its inaccessibility (Elías 1979; Rojas et al. 2003).

The fibre content of coffee pulp is high. Cellulose accounts for most of the pulp fibres, but lignin and pectin are also found in considerable amounts. Contrastingly, hemicellulose is found in low amount in coffee pulp. The use of the pulp on the diet of mice has been reported to promote health benefits, such as reduction of the absorption of cholesterol and bile salts and inhibition of pancreatic lipase (Cañas et al. 2021).

3.5.3 Potential of Coffee Pulp as a Source of Pectins

The total pectic substances in coffee pulp have been reported to be 7–15% on a dry matter basis (Reichembach and Petkowicz 2020; Wilbaux 1956). As raw material for pectin production, coffee pulp is similar to apple pomace, which contains 10–15% pectin (Rolin 1993).

As expected, the composition and molecular features of coffee pulp pectin are highly dependent on the extraction conditions (Table 3.4). Due to the presence of natural microorganisms with the potential of degrading organic compounds, the

Table 3.4 Yield and chemical characteristics of pectins extracted from coffee pulp under different conditions

Extraction conditions	Yield (%)	GalA (%)	DM (%)	DA (%)	References
Boiling HCl, pH 2, 60 min	4	91	24	n.d.	Garcia et al. (1991)
6% HMP, 1:25 w/v, 80 °C, 90 min	n.d.	n.d.	94	n.d.	Rakitikul and Nimmanpipug (2016)
HCl, 1:35 w/v, pH 2, 90 °C, 60 min and NaOH, pH 12, room temperature, 60 min	n.d.	65	100	97	Otalora (2018)
Citric acid, 1:20 w/v, pH 4, 85 °C, 125 min	8	n.d.	13 [a]	n.d.	Hasanah et al. (2019)
Boiling 0.1 M HNO_3, 1:25 w/v, 30 min	15	81	63	6	Reichembach and Petkowicz (2020)
HNO_3, 1:2 w/v, pH 3, 90 °C, 180 min; sequential extraction: citric acid, 1:2 w/v, pH 3, 90 °C, 180 min and 0.5 M NaOH, 1:1 w/v, 30 °C, 60 min	9–16	n.d.	29–62	n.d.	Chamyuang et al. (2021)
Direct precipitation of aqueous pulp, temperature and time not informed	7	54	6[a]	n.d.	Manasa et al. (2021)
Citric acid, 1:25 w/v, pH 2.7–3.5, 36–84 °C, 42–258 min	1–18	n.d.	n.d.	n.d.	Dao et al. (2022)

HMP sodium hexametaphosphate, *n.d.* not determined, *GalA* galacturonic acid, *DM* degree of methyl esterification, *DA* degree of acetylation
[a] Methoxyl content (%)

processing after collecting the material and the storage conditions also have an important role in the final quality of the pectin (Gaime-Perraud et al. 1993; Roussos et al. 1995).

A LM pectin with high level of GalA was obtained from *C. arabica* pressed pulp using HCl at pH 2 for 1 h, after purification with hexadecyltrimethylammonium bromide. Despite the high purity of the pectin, gelation was not achieved with calcium or sucrose and low pH (Garcia et al. 1991). Most studies have also not demonstrated the gelling properties of coffee pulp pectin. It was only recently that a pectin from the pulp of *C. arabica* has proven to be able to gel through the acid-induced mechanism. Acid extraction conducted with 0.1 M HNO_3 for 30 min gave rise to a HM pectin with 80% GalA on the ash and moisture-free mass, in agreement with the standard set by FAO and EU. Gelation was achieved in different concentrations of pectin, sucrose and xylitol at various pH (Reichembach and Petkowicz 2020).

The high amount of phenolic compounds in coffee pulp can be seen as a problem, since it hampers the use as fertilizer and animal feeding. Nevertheless, it can also motivate the extraction of this compound for different applications. A process for simultaneous recovery of pectin and polyphenols was proposed by Manasa et al.

(2021). Phenolics were also described to be present in the pectins extracted from coffee pulp (Reichembach and Petkowicz 2020; Manasa et al. 2021).

A method that took advantage of the presence of phenolic compounds on coffee pulp pectin has been patented. Various enzymatic treatments have been proposed for the functionalization of the pectin focusing on the transformation of phenols. The method describes the obtention of pectin by acid and alkaline extractions, followed by an enzymatic treatment to cross-link pectin chains. The patent suggests the use of peroxidase/H_2O_2 and/or laccase to form polyphenol cross-links (Otalora 2018).

Coffee pulp and its derived products have also been used for the development of sustainable plastic formulations for food packaging. The use of coffee pulp in its crude form is interesting because it is easy and cheap. However, its application is often difficulted by the low compatibility of coffee pulp with the polymeric matrix. Therefore, the use of derived products from the pulp, as pectins, can be a better option (Oliveira et al. 2021). Biodegradable films made with pectin from coffee pulp were described to have smooth surface, high transparency and good texture properties. The incorporation of microcrystalline cellulose from the pulp recovered from the solid residue after pectin extraction to the films has been used for reinforcement of the material (Dao et al. 2022).

It is probably a matter of time before coffee pulp can be used for more profitable uses. In fact, some of them have already started. The company Pectcof based on the Netherlands launched the product Dutch Gum, a pectin/protein compound obtained from coffee pulp to use as stabilizer and emulsifier. It operates in Europe, and the pulp is imported from Costa Rica and Colombia, showing that a factory can function even in nonproducing countries (Circular Conversations 2020, 29 November 2021; Pectcof 2021, 29 November 2021).

3.6 Soybean Hull

Soybean hull is a by-product from the processing of soybean (*Glycine max* (L.) Merr.), the dominant oilseed in world market and the largest plant source of edible oil and protein in animal feed (Torkamaneh et al. 2021). Brazil recently surpassed the USA in soy production, ranking first with 135 million tonnes of the grain (Embrapa, 23 Nov 2021). For the hull, estimates show that world production can be of 30 million tonnes per year (Reichembach and Petkowicz 2021).

The morphology of soybean seed, as many Fabaceae species, consists of a seed coat or hull and a large embryo, formed of cotyledons, hypocotyl and epicotyl (Fig. 3.6). The embryo is rich in protein and oil, the major products from soybean processing. The seed coat or hull is marked with a *hilum* and protects the embryo from pathogens. If the hull is cracked, seed germination will hardly happen (Liu 1997). The hull represents about 8% of the seed, and the material is rich in complex carbohydrates, making it an interesting source of dietary fibre (Gnanasambandam and Proctor 1999). However, in soybean meal, the presence of hulls diminishes the protein content (on average, decreases from 48 to 44%). A high-protein soybean

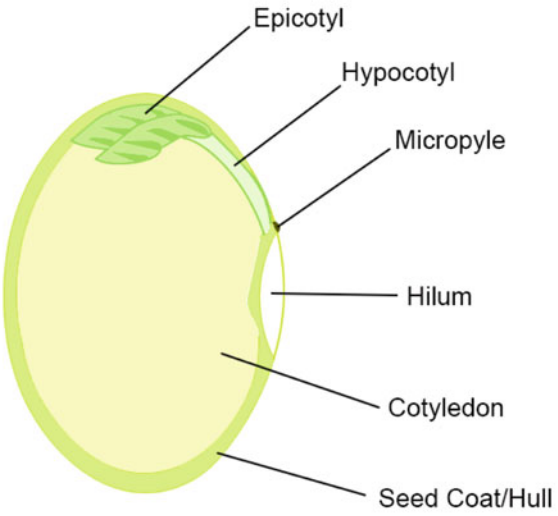

Fig. 3.6 Schematic representation of a longitudinal section of soybean and its constituents

meal is most requested from the market and consequently more expensive. Therefore, the vast majority of soybeans today are dehulled, a process called decortication, making soy hull a cheap by-product of soybean processing industries (Johnson 2008).

3.6.1 Soybean Processing and By-Products

Soybean oil has become a very popular oil for the manufacture of a wide range of food products due to its improved flavour and emulsion stability. It can be extracted mechanically or by the use of solvents. Mechanical extraction of soybean oil is often used only by small companies. The reason is that the initial investment is low, but low oil yields are obtained, which ends up restricting profits. Dry extrusion cooking of whole or dehulled soybeans disrupts the cell structure of cotyledons, allowing about 70% of the total oil to be recovered by a screw press (Ali 2010).

However, the majority of soybeans are processed by solvent extraction procedure. This process separates the oily fraction from the protein-carbohydrate-fibre meal (Blasi et al. 2000). A typical soybean oil solvent extraction is shown in Fig. 3.7.

Processing starts with the cleaning of soybean, which occurs on the farm, prestorage and before extraction. The seeds pass through magnets in order to remove ferrous metal pieces and scalping equipment to separate mud, dirt, sticks, plastic and dust. The removal of stems and leaves is critical because they can transmit moisture to the stored seeds, which should not exceed 13.0%. Air-drying is used for minor

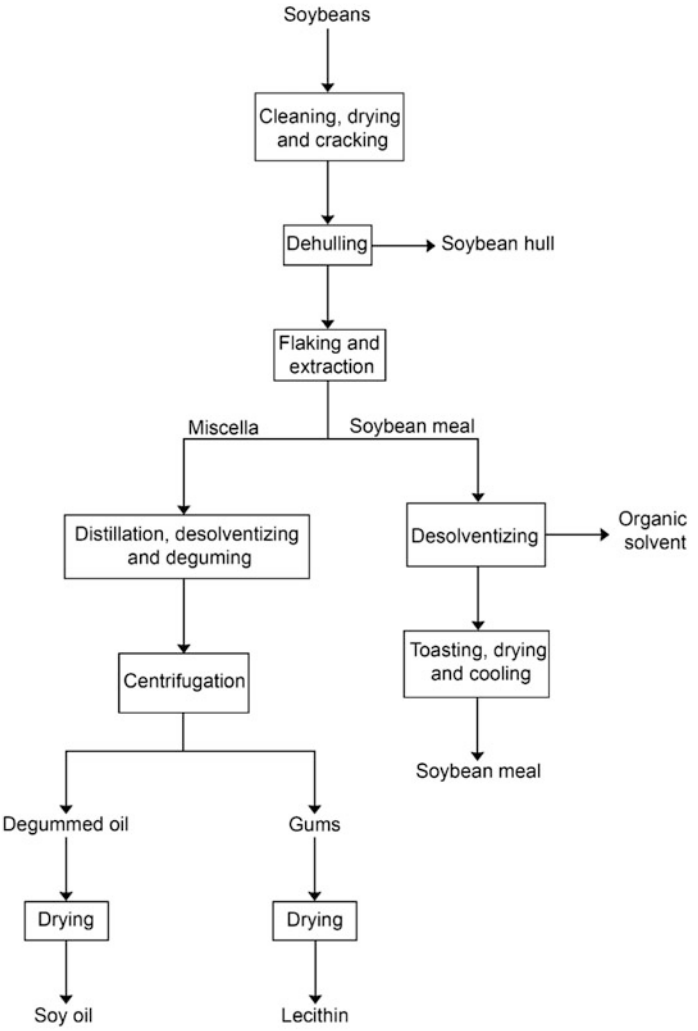

Fig. 3.7 Main steps of soy hull industrial processing and its products and by-products. (Adapted from Blasi et al. (2000))

moisture reduction of soybean, while fuel drying is required for larger reduction. Temperatures above 76 °C should not be used in the drying process (Lusas 2004). The beans then follow to the cracking step where they are broken down to a size of 0.3–0.4 cm, allowing the hull to be removed from the seed by aspiration. The hull fraction is toasted to denature urease, grounded and pelleted if desired. Pelletizing of soy hull is commonly used to reduce costs with transportation (Blasi et al. 2000).

The soybean meal coming from the dehulling step follows to the flaking process. This is performed in flaking mills, a pair of large smooth-surfaced rolls that applies pressure by mechanical or hydraulic system to generate the flakes. Flake thickness can be controlled by adjusting the pressure between the rolls (Woerfel 1995). Oil is extracted from the flakes with organic solvent, usually hexane, even though the use of isohexane has been gaining ground. The mixture of oil and solvent, known as miscella, is degummed to separate lecithin from the oil, and the latter can be refined to products as cooking oil, margarine and shortening. The remaining defatted flakes are desolventized under vacuum with supplemental heat given by steam injection, which condenses and allows the toasting/cooking of the meal, reducing urease and trypsin inhibitor activities. Leaving this step, the flakes are now referred as soybean meal and undergo toasting, where moisture is reduced from 18 to 12%. The resulting meal is finally formulated according to the specifications of the aimed final product (Blasi et al. 2000; Lusas 2004). The hulls can be added to the meal to help achieving the proper specifications or grinded and/or pelletized to be sold. Pelletizing the hulls has the advantage of increased density, decreasing costs with transportation (Blasi et al. 2000).

3.6.2 Composition and Uses of Soy Hull

After lupin, soybean stands out as the largest source of protein among legumes, with a content of 34–48%. The values vary depending on the genotype, growing environment and cultural practices of the crop (Kumar et al. 2010). The seed coat, however, presents less protein levels, in the range of 7–15%. Cystine, tyrosine and phenylalanine have been found as the major amino acids present in soy hull (Zhong and Zhao 2015). As the hulls are poorer in protein than the meal, part of them can be introduced to the final formulation, helping standardizing the product by lowering the amount of protein (Blasi et al. 2000). The contents of protein and other compounds present in soy hull are shown in Table 3.5.

Phenolics are found in low proportions in soy hull (0.2–1%) but in a substantial variety. Phenolic acids (gallic, syringic and ferulic), anthocyanins, stilbenes and isoflavones have been identified in the hulls. The flavonoids catechin, epicatechin and quercetin have also been reported to be present. Genistein and daidzein, two of the soy isoflavones, have been identified in the alkaline extract of soy hull in their aglycone form (Cabezudo et al. 2021). The aglycone form is the most relevant regarding absorption and functional properties in humans, which include prevention and treatment of various types of cancer, reduction of cardiovascular diseases, oestrogen-like activity, antiatherogenic effect and antimicrobial properties (Cabezudo et al. 2021; Isanga and Zhang 2008; Izumi et al. 2000).

Lipid content of soybean hulls varies from 1 to 5%, the major fatty acids being linoleic (50%), oleic (19%), palmitic (14%), linolenic (10%) and stearic (5%) present in the hull (Zhong and Zhao 2015). This oil composition profile is very similar to the one of soybean oil, which have been reported to be composed of the same fatty acids

Table 3.5 Chemical composition of soy hull

Component[a]	Mass fraction (%)[b]
Moisture	8.0–9.3
Protein	7.3–17.2
Lipids	0.6–4.6
Ash	4.0–5.8
Carbohydrates	79.5
Dietary fibre	42.8–76.9
Cellulose	29.0–56.4
Hemicellulose	10.2–25.0
Pectin	4.2–28.0
Lignin	1.0–12.6
Total phenolics	0.2–0.7[c]

[a] From Alemdar and Sain (2008), Cabezudo et al. (2021), Hernandez et al. (2022), Kalapathy and Proctor (2001), Liu and Li (2017), Kim et al. (2015), Mielenz et al. (2009), Monsoor (2005), Niño-Medina et al. (2017), Rojas et al. (2014), Zambom et al. (2001), Zhong and Zhao (2015)
[b] Expressed as % of gallic acid equivalents
[c] Based on the dry weight of soy hull, except for moisture

in different proportions—linoleic (55%), oleic (18%), linolenic (13%), palmitic (10%) and stearic (4%). This constitution usually results in low oxidative stability due to the high proportion of the polyunsaturated fatty acids linoleic and linolenic acids (Clemente and Cahoon 2009).

Soy hull stands out as an easily degradable material with high content of fibre. The high degradability is partially due to the low content of lignin (Mielenz et al. 2009). The low presence of lignin positively contributes for soy hull to be used in animal feed, such as for equines and aquatic animals (Coverdale et al. 2004; Aksoy et al. 2022). Also, as lignin is a major hindrance for enzymatic hydrolysis of biomass, the hulls present a good potential for saccharification and production of value-added products, such as bioethanol, butanol, enzymes, plant growth hormones, prebiotics, probiotics, polyols and organic acids (Bittencourt et al. 2021; Liu and Li 2017). Glucose (38%), xylose (10%), mannose (7%), arabinose (5%), galactose (4%) and galacturonic acid (4%) are the major monosaccharides found in the hulls, which constitute the carbohydrate portion of the fibres (Hernandez et al. 2022). Cellulose accounts for most of them, which justifies the high presence of glucose in soy hull (Table 3.5). The other monosaccharides come from hemicelluloses and pectin. Xylans containing 3–4% of D-glucopyranosyluronic acid (Aspinall et al. 1966, 1967) and galactomannans (Aspinall and Whyte 1964; Whistler and Saarnio 1957) have long been identified as soy hull hemicelluloses. Regarding soy hull pectins, several studies have focused on the extraction, characterization and uses of the biopolymer, which is discussed in the next section.

3.6.3 Soy Hull as a Source of Pectin

The low moisture content (Table 3.5) of soy hull makes it a very attractive feedstock for pectin production, since it can be stored and transported without previous drying. Citrus peel, for example, has to be dried from a moisture level of 82 to 10–12%, in order to avoid degradation by pectinolytic enzymes and fermentation by microorganisms. The energy requirement for the desiccation process is high and substantially raises the costs for manufacturing (Ciriminna et al. 2015; Kalapathy and Proctor 2001).

The first study devoted to soy hull polysaccharides was published in 1957 (Whistler and Saarnio 1957), but pectins were only isolated in 1999 (Gnanasambandam and Proctor 1999). Since then, several studies have focused on the characterization of soy hull pectic polymers (Table 3.6). Extraction with hydrochloric acid has been the most used method. However, the results are contradictory. Some reports described high yields (up to 28%) and galacturonic acid content (up to 84%) (Kalapathy and Proctor 2001; Kim et al. 2015), while others found lower values (6–12% yield and 18–39% GalA) (De Moura et al. 2017; Hernandez et al. 2022; Porfiri and Wagner 2018; Porfiri et al. 2016). Microwave-assisted extraction has been used for the extraction of pectin from soy hull, but the galacturonic acid values obtained were also low (Liu et al. 2013; Mohtashamy and Ashtiani, 2010; Wang et al. 2019; Yang et al. 2020). Poor galacturonic acid pectic fractions rich in mannose and galactose probably contain galactomannan as contaminant (Porfiri and Wagner, 2018; Porfiri et al. 2016). Considering the literature, HM and LM pectins can be obtained from soy hull (Monsoor and Proctor 2001; Porfiri et al. 2016; Porfiri and Wagner 2018).

Differences of the literature may be related to distinct procedures for pectin extraction, storage conditions of the raw material and variations of soybean genotypes. Storage conditions are critical, since physiological changes in the cytosol, cell wall and membrane can take place in the postharvest plant cell (Galindo et al. 2004). Changes in the cell wall pectins during storage were demonstrated for carrots (Ng et al. 1998). The cultivar may also affect soybean chemical constitution. The analysis of different soybean cultivars introduced for the past 50 years in Brazil has shown an upward trend in oil concentration and a downward trend in protein levels over these years (Uburanas et al. 2022). Chinese and US soybean cultivars have also clear differences in their chemical composition. US cultivars have higher levels of oil, sucrose, soluble sugars and isoflavones, while Chinese ones are richer in protein (Azam et al. 2021). Even though there are no studies evaluating these differences specifically for pectin in soy hull, it is fair to assume that variations may also occur for this polysaccharide.

Differently from commercial citrus and apple pectins, soy hull pectin presents high protein content (up to 18%) (Kim et al. 2016). A source of high-protein pectin that is used commercially is sugar beet, resulting in a product with excellent emulsifying properties. Proteins and pectins act synergistically to prevent the coalescence of droplets providing stabilization of emulsions (Funami et al. 2011;

Mendez et al. 2021). Stabilization of emulsions by pectin/protein from soybean hulls has been observed. The emulsion stability provided by soy hull pectin is similar to commercial sugar beet pectin, with superior foaming properties. The high levels of hydroxyproline have been related to its emulsifying activity (Liu et al. 2016). Plant cell wall glycoproteins that contain hydroxyproline probably are involved in the emulsion stabilization (Showalter et al. 2016). Soy hull pectin successfully stabilized fine oil-in-water emulsions during storage for 28 days (Porfiri et al. 2016) and helped reducing cooking loss and improving textural properties in meat emulsions (Kim et al. 2015, 2016).

Solutions of pectins at concentration 3% have shear thinning behaviour (Monsoor and Proctor 2001; Monsoor 2005), and the viscosity is highly influenced by the solvent (Yang et al. 2020). However, although some results have shown that soy hull can be used for pectin extraction, no study was performed to evaluate its gelling

Table 3.6 Yield, chemical characteristics and properties of pectins extracted from soy hull under different conditions

Extraction conditions	Yield (%)	GalA (%)	DM (%)	References
Sequential extraction: 1:20 w/v, 90 °C, 40 min; 0.1 M HNO_3, 0.5% HMP and 0.05 M NaOH	15	66–77	4[a]	Gnanasambandam and Proctor (1999)
0.05–0.3 M HCl, 1:3 w/v, 90 °C, 45 min	12–28	68–72	53–60	Kalapathy and Proctor (2001)
0.05 M HCl, 1:10–1:25 w/v, 90 °C, 60 min	8–16	63–69	17–21	Monsoor and Proctor (2001)
0.05 M HCl, 1:10 w/v, 90 °C, 60 min	16–21	67–69	18–20	Monsoor (2005)
HCl 1:20 w/v, pH 1.5–2.0, MRI 450–720 W, 3–6 min	9–22	24–40	68–76	Mohtashamy and Ashtiani (2010)
0.6% ammonium oxalate, 1:25 w/v, 95 °C, MRI 450 W, 10 min	n.d.	15	23	Liu et al. (2013)
0.1 M HCl, 1:10 w/v, 90 °C, 60 min	n.d.	84	n.d.	Kim et al. (2015)
0.1 M HCl, 1:3 w/v, 90 °C, 45 min and 2% HMP, 1:30 w/v, pH 4.5, 25 °C, 30 min	17–30	65–69	43–56	Liu et al. (2016)
0.1 M HCl, 1:10 w/v, 90 °C, 60 min	n.d.	64–84	n.d.	Kim et al. (2016)
0.1 M HCl, 1:15 w/v, 90 °C, 45 min	n.d.	25	78	Porfiri et al. (2016)
0.1 M HCl, 1:7 w/v, 90 °C, 45 min	6	18	69	De Moura et al. (2017)
0.1 M HCl, 1:15 w/v, 90 °C, 45 min	5–12	23	78	Porfiri and Wagner (2018)
0.6% ammonium oxalate, 1:25 w/v, 95 °C, MRI 450 W, 10 min	n.d.	48	n.d.	Wang et al. (2019)
0.6% ammonium oxalate, 1:20 w/v, 85 °C, MRI 450 W, 30 min	n.d.	47	n.d.	Yang et al. (2020)
0.1 M HCl, 1:20 w/v, 90 °C, 60 min	9	39	34–36	Hernandez et al. (2022)

HMP sodium hexametaphosphate, *MRI* microwave radiation intensity, *n.d.* not determined, *GalA* galacturonic acid, *DM* degree of methyl esterification

[a] Methoxyl content

properties under conditions used for commercial pectins. This gap clearly demonstrated the need for further studies on the potential of soy hull as a source of pectin. On the other hand, the high amount of protein in soy hull pectic polysaccharide places soy hull as a potential source of emulsifying agents.

3.7 Grape Pomace

Winemaking dates back several millennia of human history. The first evidence of winemaking—representations of the grape pressing process and wine residues in amphorae—was found in Egypt around 5000 years ago. However, there are records of archaeological artefacts containing residues compatible with wine from around 8000 years ago, found in the South Caucasus, a geographic region that today corresponds to Georgia, Armenia and Azerbaijan (Jackson 2020).

Today, grape is the fifth most produced fruit in the world, with a total production of more than 77 million of tonnes in 2019 (STATISTA, 15 Dec 2021a). It is consumed *in natura* and used for the preparation of juices, jellies, candies and raisins, but the main destination of the cultivated grapes (about 80% of the total harvesting) is the production of wines (Maroun et al. 2017).

Spain is the country that most grows grapes for wine production (13.1%), followed by France (10.9%), China (10.7%) and Italy (9.8%), considering the total area of harvesting. But when it comes to wine production, Italy, France and Spain are, respectively, the largest producers in the world. Together, they produced 136.4 million of hectolitres in 2020, which corresponds to more than a half of the world production of wine (260 million of hectolitres) (OIV, 15 Dec 2021). The production and consumption of wines also represents an important aspect for the economy, moving a large financial market in growing expansion. In 2020, the export of wines had a turnover of around €30 billion (OIV, 15 Dec 2021).

3.7.1 Winemaking Process and Grape Pomace Waste

Most wines are made from two species of grapes: *Vitis labrusca*, from which table wines are obtained, and *V. vinifera*, which are used to produce fine wines (Arcanjo et al. 2017). According to the colour of the skin, resulting from the accumulation of anthocyanins, grapes are classified as white or red (or black) (Massonet et al. 2017). Wines are also classified according to colour, such as white, red or rosé wines, but this is not necessarily related to the colour of the grape used for winemaking; it is even possible to obtain white wines from red grapes (Bruch 2012). The difference between white wines and red wines is the manufacturing process, particularly the fermentation step, as can be seen in Fig. 3.8. Red wines are produced by the alcoholic fermentation of the must in the presence of the solid parts of the fruit, such as skins and seeds, and pressing occurs only after fermentation; this is the stage

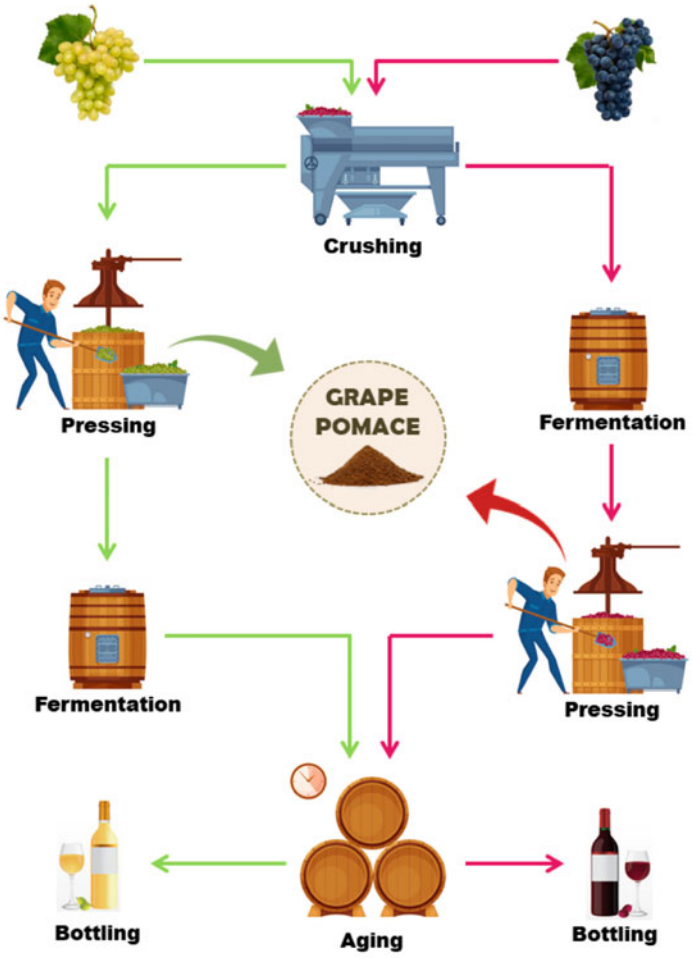

Fig. 3.8 Steps of winemaking process. For production of white wines, grapes are crushed and then pressed for separation of the grape pomace and the juice, which is then fermented. On the other hand, red wines are produced by fermentation of the whole fruits crushed, and only at the end of fermentation step the material is pressed and the grape pomace is generated. (Adapted by the authors from Freepik and Vecteezy, under free license)

in which the pomace is separated. In the manufacture of white wines, the fruits are pressed, the solid parts are removed and only the juice is fermented, and thus the pomace does not undergo the fermentation (Bruch 2012; Iannone et al. 2016).

From the pressing step, besides a large volume of a greatly appreciated drink and a large amount of money, winemaking also produces a large amount of waste. About 20% of the initial weight of the fresh fruits remains as waste after the processing (Domínguez et al. 2017), which represents an annual production of around 12 million

tonnes of winemaking waste. This waste, referred as grape pomace or grape marc, is composed of skins, seeds and sometimes stalks, depending on the processing type. When stalks are not removed prior to the pressing process, they may account for up to 30% of the grape pomace, whereas seeds and skin represent, respectively, about 30 and 40% (Domínguez et al. 2017).

3.7.2 Composition and Uses of Grape Pomace

The composition of grape pomace varies depending on the grape variety, the viticulture practices and the winemaking process. Moisture varies greatly according to the pressing conditions (Moreno et al. 2020). Proteins, lipids and a great diversity of phenolic compounds make up the grape pomace, but the main components are the dietary fibres (Table 3.7) (Sirohi et al. 2020; Moreno et al. 2020).

The grape pomace is mainly used as fertilizer or for animal feed. However, both uses have some drawbacks. The disposal of large quantities of pomace in the soil can alter the physical and chemical properties as well the microbiome due to the presence of organic acids that can decrease the pH, high amounts of heavy metals, the presence of phytotoxic polyphenols and substances with antimicrobial activity (Bustamante et al. 2005; Domínguez et al. 2017).

The use of grape pomace in animal feed can bring some benefits when used as a diet supplement, due to the presence of antioxidant species and dietary fibres (Zhao et al. 2018; Kafantaris et al. 2018). However, the high amount of lignin and tannins present in grape pomace can hinder the digestion of this material, limiting its use as a source of energy and affecting the digestibility and absorption of nutrients (Nistor et al. 2014; Antonic et al. 2020). Therefore, it must be implemented in the animal diet only in low amounts (Nistor et al. 2014).

A possible use of grape pomace for biofuel production has been proposed. As it is mostly composed of carbohydrates, from the fermentation of the material, it is possible to obtain bioethanol, biogas and biobutanol. The production of biodiesel by transesterification of oil extracted from grape seeds has also been proposed (Sirohi et al. 2020). However, the seeds account for only 28% of the waste, with an oil content of 13–19%. Methane is another product that could be obtained by anaerobic fermentation of grape pomace, to be used as a source of energy (Dávila et al. 2017).

However, one of the most profitable ways of reusing grape pomace is the use as a source of bioactive compounds and molecules for different industrial applications. These compounds include phenolics, such as hydroxycinnamic acids, flavanols, flavonol glycosides, which are present mainly in the seeds, and anthocyanins, which are abundant in the skins of red varieties but not in the white ones (Kammerer et al. 2004); organic acids, mainly tartaric, malic and citric acid (Sirohi et al. 2020); tannins (Ping et al. 2011); and dietary fibres, well known for its beneficial health effects (Zhu et al. 2015).

Table 3.7 Chemical composition of grape pomace

Component[a]	Mass fraction (%)[b]
Moisture	50.2–72.2
Protein	9.29–13.84
Lipids	7.61–10.47
Ash	3.21–6.86
Dietary fibre	36.92–51.82
Total phenolics[c]	7.5–14.7
Gallic acid	0.1–0.7
Caffeic acid	0.04–0.1
(+)-Catechin	0.3–0.8
Ferulic acid	0.9–1.9
Synergic acid	3.1–7.1
Protocatechin	9.8–16.8
Quercetin	0.007–0.04
Rutin	0.1–0.3
Kaempferol	0.1–0.4
Chlorogenic acid	15.3–29.6
Mineral content	
Ca	0.3–0.8
K	1.2–2.7
P	1.6–3.2
Mg	0.2–0.6
Mn	0.8–1.4
Na	0.1–0.2
S	0.1–0.2
Cu	0.1–0.2
Fe	2.1–5.5
Zn	1.3–2.2

[a] From González-Centeno et al. (2010) and Ahmed et al. (2020)
[b] Based on the dry weight of grape pomace, except for moisture
[c] Expressed as % of gallic acid equivalents

3.7.3 *Dietary Fibres from Grape Pomace*

The dietary fibres encompass the cell wall polysaccharides and lignin (Hamaker and Tuncil 2014). They are the main components of the grape pomace, and the fibre content depends on grape variety (Table 3.8).

A qualitative estimate of the kind of polysaccharides present in the grape pomace can be obtained from the monosaccharide composition of the plant material. Results from different research laboratories show that the amount and proportion of monosaccharides found in the grape pomace varies with the grape variety, colour and the region where the grapes are harvested (Table 3.9).

It seems that white grape pomaces have higher amounts of uronic acid, but lower carbohydrate content, compared to the red ones. Despite the differences, in general,

Table 3.8 Total dietary fibre content (TDF) of different varieties of grape pomace

Grape species	Grape variety	Red/white	TDF (%)	References
V. vinifera	Morio Muscat	White	17	Deng et al. (2011)
	Muller Thurgau	White	28	
	Merlot	Red	51	
	Cabernet Sauvignon	Red	53	
	Pinot Noir	Red	56	
V. vinifera	Airén	White	80	Valiente et al. (1995)
V. vinifera	Malbec	Red	66	Bender et al. (2020)
V. vinifera	Cabernet Sauvignon	Red	82–86	Zhu et al. (2012)
V. vinifera	Benitaka	Red	47	Sousa et al. (2014)
V. vinifera	Manto Negro	Red	74	Llobera and Cañellas (2007)
V. vinifera	Prensal Blanc	White	72	Llobera and Cañellas (2008)
V. vinifera	Merlot	Red	48	Iora et al. (2015)
	Tanat	Red	44	
	Cabernet	Red	52	
V. vinifera	Cabernet Sauvignon	Red	26	Ribeiro et al. (2015)
V. vinifera	Merlot	Red	59	
V. labrusca	Mixture[a]	Red	57	
V. labrusca	Terci	Red	58	
V. labrusca	Bordeaux	Red	64	Karnopp et al. (2017)

[a] Mixture refers to a cluster of Bordeaux (65%), Isabel (25%) and BRS Violet (10%) (Ribeiro et al. 2015)

the main monosaccharides present in grape pomace are glucose, uronic acids and xylose, suggesting the presence of cellulose, xyloglucans and pectic polysaccharides.

3.7.4 The Potential of Grape Pomace as Source of Pectins

Although grape pomace is an abundant residue rich in pectic polymers, only a few studies have focused on its potential as an alternative source for commercial production of pectin. Most of the investigations performed with grape pomace used approaches that are not related with the industrial procedures used for pectin production (Table 3.10). In these studies, the pectin was isolated from grape pomace using different extraction techniques, which hampers the comparison among the different varieties of grape.

The comparison among the studies that used the same extraction and characterization approaches shows differences in the pectin content and features among the different grape varieties. In general, red grape pomace tends to provide higher pectin yields than white grape pomace. However, even among varieties of the same colour, the pectin amounts are quite variable.

Table 3.9 Carbohydrate content, monosaccharide composition and possible polysaccharides present in different grape pomaces

Grape variety	Red (R)/ white (W)	Harvest region	Carbohydrates (%)	Monosaccharide composition (%)								Possible polysaccharides present	References
				Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA		
Mixture of Pinot Noir, Riesling, Sylvaner, Muscat and Gewurztraminer	Both	Alsace (France)	37	1	1	4	12	7	5	58	12	Glucans, xyloglucans and lower amounts of pectins	Rondeau et al. (2013)[a]
Mixture of Sauvignon, Semillon, Cabernet Sauvignon and merlot/Ugni blanc	Both	Aquitaine (France)	46	1	tr	5	7	10	6	57	14		
Gamay	R	Beaujolais (France)	21	1	tr	3	11	10	6	58	11		
Mixture of Chardonnay and Gamay	Both	Bourgogne (France)	32	2	tr	5	7	10	7	51	18		
Mixture of Chardonnay and Pinot	W	Champagne (France)	36	1	tr	5	19	5	5	51	13		
Mixture of Clairette, Carignan, Merlot, Grenache	Both	Languedoc (France)	30	1	1	2	11	10	6	59	10		
Mixture of Muscadet, Chardonnay, Cabernet Sauvignon	Both	Val de Loire (France)	19	2	tr	5	8	10	7	51	17		
Mixture of Clairette, Ugni Blanc, Semillon	W	Provence (France)	32	1	tr	4	12	9	6	55	13		
Cabernet Sauvignon	R	Spain	24	tr	tr	5	12	7	4	41	31	Mainly pectins and cellulose	González-Centeno et al. (2010)[b]
Callet			30	tr	1	5	17	6	3	38	30		
Manto Negro			23	tr	tr	7	11	6	5	39	32		
Merlot			28	tr	tr	6	19	7	3	35	30		
Syrah			29	tr	tr	5	18	6	4	38	29		
Tempranillo			32	tr	tr	5	13	5	4	38	35		

Chardonnay	W		19	tr	tr	6	14	5	4	30	41		
Macabeu			16	tr	tr	6	8	6	4	36	40		
Parellada			24	tr	tr	7	12	6	4	39	32		
Prensal Blanc			17	tr	tr	6	11	5	4	36	38		
Cabernet Sauvignon	R	Murcia, (Southeast Spain)	28	2	tr	6	3	6	5	42	36	Pectins, glucans and xyloglucans	Apolinar-Valiente et al. (2015) [b]
Syrah			26	2	1	6	4	5	5	45	32		
Monastrell			32	2	tr	7	4	6	7	40	34		

Rha rhamnose, *Fuc* fucose, *Ara* arabinose, *Xyl* xylose, *Man* mannose, *Gal* galactose, *Glc* glucose, *UA* uronic acids, the sum of galacturonic acid and glucuronic acid, *tr* traces (<0.5%)

[a] From the dry pomace

[b] From the AIR

Table 3.10 Yield and chemical characteristics of pectins extracted from different grape pomaces under different conditions

Grape variety	Red (R)/ white (W)	Harvest region	Extracted material	Extraction conditions	Yield (%)	GalA (%)	DM (%)	References
n.d.	n.d.	Spain	80% phenol and DMSO pretreated DP	Sequential extraction: 50 mM CDTA pH 6.5; 50 mM Na_2CO_3 + 20 mM $NaBH_4$	1 (CDTA)	89	5 (CDTA)	Müller-Maatsch et al. (2016)
					1 (Na_2CO_3)	32		
Merlot	R	South Brazil	DP	Phosphate-citrate buffer, pH 3.0, 1: 50 (w/v), 80 °C, 2 h	7	n.d.	n.d.	Iora et al. (2015)
Tanat					5			
Cabernet Sauvignon					3			
Muller Thurgau	W	Northwest USA	DP	Sequential extraction: H_2O; 20 mM EDTA; 50 mM NaOH	n.d.	~0.1 (water)	n.d.	Deng et al. (2011)
						~4 (EDTA)		
						~0.1 (NaOH)		
Morio Muscat						~0.1 (water)		
						~3 (EDTA)		
						~0.04 (NaOH)		
Cabernet Sauvignon	R					~0.1 (water)		
						~5 (EDTA)		
						~0.1 (NaOH)		
Merlot						~0.5 (water)		
						~4 (EDTA)		
						~0.1 (NaOH)		
Pinot Noir						~0.2 (water)		
						~4 (EDTA)		
						~0.1 (NaOH)		

Cabernet Sauvignon	R	South Russia	DP	Extraction method not described; isolation of pectins by calcium precipitation (PP) and by ethanol precipitation (WSP)	2 PP	~41	65	Limareva et al. (2020)
					1 WSP			
Saperavi North	R				3 PP	69	52	
					2 WSP			
Moldova	R				4 PP	57	65	
					2 WSP			
Aligote	W				2 PP	~39	64	
					1 WSP			
Chardonnay	W				2 PP	~50	54	
					1 WSP			
Rkatsiteli	W				2 PP	~40	55	
					1 WSP			
Firstborn Magaracha	W				3 PP	~40	62	
					1 WSP			
Cabernet Sauvignon	R	Spain	DP	Response surface method, ultrasound-assisted extraction, citric acid, pH 2, 75 °C, 60 min	32	~97	55	Minjares-Fuentes et al. (2014)
Chardonnay	W	South Brazil	AIR	Response surface method, boiling HNO_3, 35.11 v/w, pH 2.08, 135.23 min	11	57	43	Colodel et al. (2020)
Fetească Neagră	R	Republic of Moldova	DP	Conventional acid extraction varying acid type (citric, H_2SO_4 and HNO_3), particle size interval (<125 μm, ≥125 to <200, ≥200 to <300), pH (1, 2 and 3), temperature (70, 80 and 90 °C) and time (1, 2 and 3 h)	6–10	33–53	72–85	Spinei and Oroian (2022)
Rară Neagră					6–8	41–55	71–75	

GalA galacturonic acid, *DM* degree of methyl esterification, *n.d.* not determined, *DP* dry pomace, *AIR* alcohol insoluble residue

Considering the results of Limareva et al. (2020), the pectins from red varieties contain more uronic acid than those from white grape pomaces, but no relationship was found with DM.

The studies by Minjares-Fuentes et al. (2014), Colodel et al. (2020) and Spinei and Oroian (2022) were devoted to the investigation of the potential of grape pomace as an alternative source for industrial production of pectin. The pomace of red grape variety Cabernet Sauvignon, cultivated in Spain, was used for the extraction of pectin with citric acid using ultrasound-assisted method (Minjares-Fuentes et al. 2014). To obtain the high yield, average molecular weight and DM, a Box-Behnken design was used to optimize the extraction process. The variables were temperature (35–75 °C), time (20–60 min) and pH (1.0–2.0). The highest yield of pectin was achieved at 75 °C for 60 min and pH 2. Under these experimental conditions, a pectin composed of >97% of GalA with average molecular weight of 163.9 kDa and DM of 55.2% was isolated with yield of 32.3%.

For white Chardonnay grape pomace, harvested in South Brazil, a central composite design was applied to the optimization of pectin extraction using conventional nitric acid extraction, aiming the highest yield and galacturonic acid content (Colodel et al. 2020). The effect of pH (1.66–3.34), extraction time (10.77–135.23 min) and liquid/solid ratio (9.89–35.11 ml/g) was evaluated. The best conditions were found to be pH 2.08, extraction time of 135.23 min and liquid/solid ratio of 35.11 ml/g. In the optimized conditions, an experimental yield of 11.1% of a LM pectin (DM of 43.3%) with 56.8% GalA was obtained.

More recently, the effect of acid type (nitric, sulphuric or citric acid), particle size (<125 μm, ≥125 to <200 μm and ≥200 to <300 μm), pH (1–3), time (1–3 h) and temperature (70–90 °C) on extraction of pectin from pomace of the two red grape varieties cultivated in Moldova was investigated (Spinei and Oroian 2022). The highest yield (7.3%), GalA content (62.21%), DM (81.4%) and molar mass (5.32×10^4 g/mol) of pectin from both grape pomace varieties were obtained by extraction with citric acid at pH 2, particle size interval of ≥125 to <200 μm and temperature of 90 °C for 3 h.

The different studies evidence the presence of pectins in grape pomace and differences between the pomace compositions among varieties. However, further investigation regarding the potential of this waste as an alternative raw material for pectin production is needed. Innovative techniques such as ultrasound-, microwave- and enzyme-assisted extraction (Maríc et al. 2018) are also encouraged to be tested to a greater extent to extract pectins from grape pomace, considering the results obtained by Minjares-Fuentes et al. (2014). In addition, the gelling properties of the pectins studied so far were not investigated.

It is also important to note that no studies were found on the pectins from pomace from grapes of *Vitis labrusca* species. Therefore, research on grape pomace pectins of both species, *V. vinifera* and mainly *V. labrusca*, has a large gap to be filled.

3.8 Conclusions

Despite the difficulties to compare the results from studies that used distinct approaches for extraction and analysis, it is clear that cocoa pod husk, coffee pulp and grape pomace can be used for industrial production of pectin. Pectins that fit the purity requirements set by the international regulatory food agencies and are able to form gels have already been extracted from these plant wastes, which are available in huge amounts. However, further studies are required to determine if soybean hulls can provide pectins with commercial features. Aspects such as location of the facilities and seasonality need to be considered to find out the best economic strategy to implement the use of these raw materials. New processing waste plants should preferably use the biorefinery model for the concomitant recovery of other value-added compounds.

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Chapter 4
Biomaterials Derived from Agricultural Waste: A Focus on Collagen

Safiya Noorzai and Casparus Johannes Reinhard Verbeek

Abstract Heightened environmental consciousness has led scientists and researchers to seek substitutes to replace petroleum-based materials in a renewable and a sustainable approach. The expansion of world's population is one of the most concerning problems the planet is currently experiencing, and by default along with the increase in population is the increase of cumulative waste from various industries. The world's population generates an overwhelming 3.6 million tonnes of municipal daily, and this value is to rise to 6.1 million tonnes daily by 2025. The waste and the emissions are in return adversely affecting health and polluting air, freshwater and ocean life. One of the best and often omitted methods of managing waste in a sustainable fashion is through waste valorisation. This waste management method can result in a number of high-value products which can be utilised in a myriad of industries. The meat production industry represents a significant number of by-products, which are untapped, from which a substantial number of invaluable proteins, fats and chemicals can be extracted and derived from. In particular, associated with the meat production industry are tanneries and rendering plants, which process bovine and other livestock hides for leather production.

Rendering processes divides animal by-products into protein meal and rendered animal fat, while tanneries seek to process hides into leather. Nevertheless, a considerable quantity of waste is still generated from these activities that can be utilised to extract and further to derive high-value products. Such high-value product is collagen. Collagen can be extracted from bovine and cattle hides, but, even better, the same collagen can be extracted from hide off-cuttings. The hide off-cuttings are generated as additional waste during the leather preparation steps. Acknowledging the soaring price of collagen and its myriad number of applications and industries it is utilised in, the extraction of such high-value product from bovine hide off-cutting

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is equally economical and sustainable. This chapter aims to present and discuss how the biomaterial collagen can be extracted from agricultural waste such as from bovine hide off-cuttings. This chapter further discusses the applications of collagen as a high-value biomaterial in various industries.

Keywords Collagen extraction · Biotechnology · Polymer engineering · Agricultural waste valorisation · Biomaterials

4.1 Introduction

Advancements in nanotechnology and biotechnology have enabled researchers to bioengineer agricultural waste and bioproducts into high-value biomaterials with diversified applications. Recently, waste valorisation methods have attracted a substantial amount of interest with the exclusive objective of waste management in the most sustainable way. By-products and waste from a variety of industries are incredibly concerning challenges that the planet is presently facing, and this will only rise with the increase in population and it needs to be addressed by the scientific community. The meat manufacturing and processing industries represent many by-products that are underutilised, from which a significant number of invaluable proteins, fats and chemicals can be extracted and derived from. Rendering and tannery plants process bovine and cattle hide mainly for production of leather. Cattle processed for meat utilisation and casualty cattle result in a significant mass of waste which includes the production of hide off-cuttings.

Tanneries generate several beneficial biological waste materials including hide shavings, hide off-cuttings and leather scrap. Due to lack of innovation and limited waste valorisation knowledge, the biomaterials generated in tanneries are disposed of in landfill sites. In return, this results in inflated landfilling costs per mass unit as this waste biomaterial has low density and little to low compression ability. To a certain degree, the waste biomaterial generated in tanneries is converted to animal feed; however, this offers minuscule or no economical or environmental value, in spite of the high and valuable biopolymer content. The corium section of the bovine hide comprises and is copious in the invaluable structural protein of collagen.

Collagen is an insoluble molecule found in the mammalian skin, cartilage, bone, connective tissue, tendons and blood vessels. Collagen acts as a structural protein and therefore provides flexibility, strength and stability in tissues in which it is found, and accordingly bovine and cattle hides are rich in collagen—specifically in the corium section of the skin. At the molecular level, collagen is made of repetition units of $(GLY\text{-}X\text{-}Y)_N$ amino acids, where GLY is the amino acid of glycine, X is often proline and Y is hydroxyproline. This repetitive structure forms three distinct alpha chains which in turn fashion into a triple helix (Shoulders and Raines 2009; Gelse et al. 2003).

Taking into consideration the exorbitant cost of collagen, the broad number of industries and purposes it can be of value, a better waste management and

sustainable alternative would be to extract as much collagen as feasible from bovine hide off-cuttings.

Collagen from bovine hides is a highly sought-after protein and thus is being utilised in regenerative medicine; collagen can be used in casings and encapsulation, in nutritional supplements, as base or an enforcement ingredient biodegradable films and coatings and in pharmaceuticals. The extracted collagen can be used for the preparation of several high-value biomaterials, including for the development of biomedical sponges, pellets for delivery of drugs, collagen shields for ophthalmology, nanoparticles for gene delivery, and for 3D printing of collagen scaffolds as a foundational and support material for the development of artificial organs.

There is immense demand for collagen as it is a highly sought-after protein. The global collagen market was estimated at $8.36 billion (USD) in 2020, and it is projected to be valued at $16.7 billion (USD) by the year 2028, raising at a compound annual growth rate of 20% (Research 2021). The market value of collagen ranges from $37/g (USD) to as high as $1000/g (USD) for lab-grade collagen (SigmaAldrich 2018).

Extracting bovine collagen over collagen from alternative sources offers numerous advantages, including a high collagen denaturation temperature in contrast to collagen from aquatic sources. The extraction of fish and specifically porcine collagen presents many constraints, while purposes of fish collagen are restricted because of the collagen's lower hydroxyproline content (Aberoumand 2012) and the use of porcine collagenous products is forbidden both in the Jewish and Muslim communities (Schmidt et al. 2016).

Waste valorisation of bovine waste materials such as bovine hides into high-value materials can enable an effective and an economical method of agricultural waste.

4.2 The Effect of Tannery Waste Materials on the Environment

The tannery and the leather manufacturing industries are considered to play a crucial role in the recycling and the reutilisation of meat industry by-products; however, the processes applied in tanneries and in the leather manufacturing industry possess a severe negative effect on the environment.

Tanneries are a cause of environmental concern as they have high resource utilisation, including vast content of chemicals, water and energy. Furthermore, the processes occurring in tanneries result in production of emissions, wastewater and waste solids. These processes also release corrosive gasses in significant amounts the release of contaminated water which often isn't treated. Additionally, the tanning process requires the removal of hide off-cuttings, fleshings and trimmings and hair. On ground, approximately no more than 25% (weight percent) of the hide results in the finished leather, meaning that the other 75% is discarded (The European IPPC Bureau 2013). The sludge and wastewater treatment of tanneries

Table 4.1 Wastes and chemicals utilised during the processing of bovine hide to finished leather production (Palacios et al. 2016)

Tannery processing step	Type of chemical	Generation of waste
Preservation of the hide		
	Salt	Hide trimmings and contaminated salt
Bovine hide soaking		
	Water, enzymes and surfactants	Wastewater (both contaminated and salt water)
Hide de-hairing		
	Enzymes, water and sodium sulphide	Hair, alkaline water
Fleshing		
	Mechanical processes and water	Wastewater and fleshings
Hide splitting		
	Mechanical processes	Raw hide trimmings
Deliming of the hides		
	Acids, water and ammonium sulphate	Acidic wastewater

produces further waste that is often harmful to the environment. Finished leather finds use in a number of applications including being of use in furniture, shoes and bags. However, the waste generated in this industry has copious potential to be utilised in economical and environmentally efficient methods. It is important to consider that bovine hides from bull-hides are often too thick process and hide thinning steps are required. The added hide thinning steps not only add cost to the overall process but also generate excess waste.

The production of bovine and cattle hides into leather requires the use of a large number of chemicals, and these chemicals are released into the environment with the generation of waste products at each step of the process. Table 4.1 gives an indication of the type of chemicals and the waste generated during the main steps of leather production.

4.2.1 The Use of Bovine and Cattle Hides for Collagen Extraction

During the transformation of bovine and cattle hide to finished leather, a significant amount of waste is generated. This waste includes bovine hide off-cuttings, defected hide parts or whole hides that are defected and not suitable for leather production and trimmings that are all rich in collagen. The hide off-cuttings are often disposed of in landfill or processed to produce animal protein feed. Animal protein feed is a low-value derivative of bovine hides post-processing costs. Collagen can be

extracted from these hide off-cuttings, including bovine hide trimmings, and bull hides that require additional thinning steps are often too thick to process as it is.

Collagen is a structural protein found in the mammalian body. This protein makes up approximately 30% of the total protein found in the mammalian body and functions to provide structural integrity, strength and stability to the tissues that it constitutes (Rizk and Mostafa 2016). Collagen is a major protein found in the mammalian skin, including in the bovine hide, specifically in the corium-rich section of the skin.

There are a number of different collagen extraction techniques that can be applied to derive collagen from bovine hides. These methods range from being efficient and resulting in high collagen yields to being inefficient, costly and resulting in low-grade collagen. Therefore, it is crucial to understand the different extraction methodologies and to work towards optimisation of methods to achieve an extraction method that is economical and environmentally friendly and one that does not contribute to the rising carbon emission rates.

4.3 Extraction Methodologies of Collagen from Agricultural Waste

The most abundant protein found in the vertebrate body is collagen. This protein in its triple-helix form is nonextensile and fibrous making it a key component of skin, blood vessels, tendons, bones, cartilage and teeth. Collagen is a structural protein, and hence it functions to provide strength to tissues in the body though it functions accordingly to where it is found in the mammalian body (Yang 2008). The content of collagen in the mammalian body is vast, and it is approximated to account as one-third of the total protein content (Shoulders and Raines 2009).

At a molecular level, collagen is comprised of three distinct polypeptide chains, which are α1, α2 and α3. The uniqueness of each of these chains is in their amino acid composition, for example, collagen type I is identified for comprising of α1 (I) and/or α2 (I) chains, and the most common variant of type I collagen triple helix consists of two α1 (I) chains and one α2 (I) chain. The repetitive order of $(GLY\text{-}X\text{-}Y)_N$ amino acids which form the triple-helical structure of collagen is further coiled around each other, and this series of three alpha chains is termed as the tropocollagen (Shoulders and Raines 2009). Collagen gains its structural functionality from the aspect that tropocollagen units are arranged as sheets and fibres. Each individual alpha chain of collagen contains approximately 1000 amino acids with the repetitive fashion of $(GLY\text{-}X\text{-}Y)_N$ amino acids. In order for collagen to achieve the correct folding of chains into the tropocollagen molecule, all the alpha chains require a glycine amino acid to be present in every third position of the polypeptide chain (Shoulders and Raines 2009). The majority or one-third of the amino acids found in collagen alpha chains is glycine. Glycine plays a very important role in the synthesis

of collagen as substitution of one single glycine for another amino acid can result in mutations and in skeletal deformities such as *ontogenesis imperfect* (Noorzai 2020).

4.3.1 Types of Collagen Found in the Mammalian Body

The protein collagen has several different functionalities in the mammalian and the aquatic tissue. The function of collagen differs based on the tissue that it constitutes. Collagen is known to be found in skin, teeth, the blood vessels, tendon, cartilage and bone. In order to have such diverse functions in a number of diverse tissues, there a number of different collagen types (type I to type XXVIII) (Noorzai and Verbeek 2020). So far, researchers have identified approximately 28 types of collagens with collagen types I–III being the most investigated and the most abundant. Though there are a vast number of different types of collagens found in the mammalian body, it is important to note that over 90% of the collagen found in the mammalian body is type I collagen. The differences amongst the different types of collagen are not variant to a great extent chemically; however, differences arise from the way the alpha chains are assembled, to the different lengths of the helix to the differences in the terminations of the helical domains (Bornstein and Helene 1980).

4.3.2 Collagen Extraction from Bovine Hides

Collagen can be extracted from several different mammalian and aquatic sources, though collagen from bovine sources is known to be the most utilised and investigated source of collagen applied in a copious array of industries ranging from the food industry to cosmetics to high-grade collagen medical applications. Bovine collagen is sourced from bovine and cattle skin, muscle, tendons and bones. Researchers in the past have attempted at extraction of collagen from bovine hides and other sources; however, bovine collagen extraction gained momentum in the 1970s when scientists developed systems and methodologies of collagen extraction and further processed this collagen into a liquid form (Armstrong 2010).

The term “bovine hide” describes the unbleached and natural skin and hair of cattle. The meat processing industry produces bovine hides as a by-product, and without complex process, the bovine hide can be transformed into leather which subsequently can be utilised in the shoe and clothing industries. However, as much as the leather manufacturing industry is described as processes without complexity, it does produce an immense amount of waste and contributes negatively to the environment.

The bovine hide consists of water (60–65%), protein (25–30%) and fats (5–10%) (Fig. 4.1). The bovine hide’s protein component is mainly collagen (approximately 90%) and some elastin (approximately 10%). The bovine hide is segmented into four main parts, including the epidermis, the grain section, the corium and flesh. The

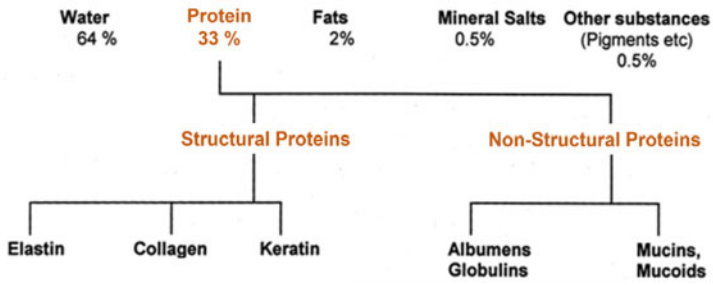

Fig. 4.1 Composition of bovine hides

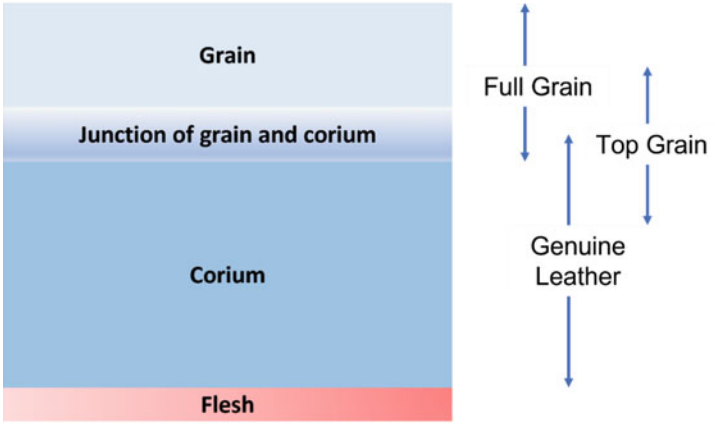

Fig. 4.2 Sections of the bovine and cattle hide

thickness of the skin and therefore the portion of each part vary all over the mammalian body.

4.3.3 Bovine Hide Properties

The sections of the bovine hide are further discussed below (Fig. 4.2):

- The epidermis: The main epidermis layer of bovine hides is a protective layer of cells, and the other bovine hide epidermis is the flesh remains that are removed during tanning and liming processes.
- The grain: Collagen and elastin are the constituents of this layer of the bovine hide. This layer is usually separated during tanning and leather manufacturing to be utilised in the cosmetic industry.

– The corium section: This section of the bovine hide is collagen-rich, and it is this section of the skin that gives skin its structural integrity and strength. The thickness of the corium section increases with age; however, after a certain age, the collagen production decreases, and this is observed in the skin of mature animals.

Extraction of collagen from bovine hides varies from researcher to researcher and company to company; however, every collagen extraction procedure must follow some standard requirements. These requirements include removal of non-collagenous protein, dissolution of collagen, precipitation of collagen, purification and lyophilisation of collagen.

Collagen extraction requires careful and methodical processes to yield high-quality collagen. Bovine hides to be utilised for collagen extraction are to be chopped in small pieces (approximately 2 cm by 2 cm); this increases the tissue extraction surface area and simultaneously speeds up the process of extraction. Prior to extraction, the temperature of the samples needs to be monitored and preferably kept at approximately 4–8 °C. Collagen denatures at the temperature range of 40–50 °C; the preference of 4–8 °C is to prevent bacterial contamination of the samples. The monitoring of the temperature is recommended to prevent unravelling of the tropocollagen and to avoid denaturation of the collagen prior to extraction. Denaturation of collagen reduces the value of the protein and limits its applications. For applications where high-grade collagen and native collagen are required, the temperature at the step of extraction process needs to be strictly monitored (Aberoumand 2012).

It is important to note that extraction processes need to be altered for collagen sources from juvenile sources such as from the skin of calves or chicken embryos. The young samples can swell and become soluble in low acid concentrations, and the collagen can be recovered via precipitation with sodium chloride (1–5 M concentrations). The concentration of sodium chloride will need to be altered for different tissues (Nalinanon et al. 2007).

Collagen from older samples has a great number of cross-linking between the tropocollagen units, and these lysine-hydroxylysine covalent bonds cannot be broken easily with low acid concentrations. The cross-linking in older tissue connects the tropocollagen units together to improve chemical resistance and structural integrity of the collagen. The number of lysine-hydroxylysine cross-linking varies from tissue to tissue, e.g. collagen found in tendons is highly cross-linked to give strength to the tissue (Ko et al. 2010). Mature collagen-containing tissue can be made soluble with the addition of enzymes such as pepsin with high concentration of an acid, such as acetic acid. The enzymes work to attack and cleave the unwound sections of the tropocollagen units, and the acid swells the tissue to allow the tropocollagen units to detangle and separate (Nalinanon et al. 2007).

The subsections that follow examine the principal criterion of collagen extraction from various sources.

4.3.4 Monitoring of Temperature

For extraction of high-quality collagen, and to avoid contamination and unravelling of the tropocollagen units, the temperatures of the entire extraction process need to be monitored (Table 4.2).

4.3.5 Demineralisation and Defatting Steps

The chosen tissue utilised for collagen extraction is often first de-haired, chopped into small pieces for greater surface area and further prepared for defatting. The sample tissue can be defatted with several chemicals found in literature such as organic solvents and detergents. Demineralisation and defatting chemicals found in literature are outlined in Tables 4.3 and 4.4.

Table 4.2 Collagen extraction temperature range used in literature

Collagen source	Temperature (°C)	References
Bovine	4 °C	Lin and Liu (2006), Park et al. (2012), Rizk and Mostafa (2016), Li et al. (2008), Zhang et al. (2006), Ran and Wang (2014)
Fish	4–9 °C	Chen et al. (2015), Kittiphattanabawon et al. (2005), Yan et al. (2008), Lin and Liu (2006), Park et al. (2012), Zhang et al. (2007), Tylingo et al. (2016), Muralidharan et al. (2013), Kiew and Mashitah (2013)

Table 4.3 Chemicals utilised for defatting of collagenous samples

Collagen source	Chemical	References
Bovine	Various concentrations of acetone	Ran and Wang (2014), Neuman and Logan (1950)
Fish	0.5% detergent	Zhang et al. (2007), Sadowska et al. (2003)
	10% Butyl alcohol	
	15% Butyl alcohol	Nagai and Suzuki (2000), Kiew and Mashitah (2013), Zhang et al. (2009)

Table 4.4 Demineralisation chemicals found in literature

Collagen source	Chemical	References
Fish	0.5 M ethylenediaminetetraacetic acid	Nagai and Suzuki (2000)
Bovine sources	0.5% Hydrochloric acid	Zhang et al. (2006)
	0.5 M Ethylenediaminetetraacetic acid	Bowman et al. (1996)

4.3.6 Elimination of Other Proteins: Non-collagenous Proteins

Post demineralisation and defatting, non-collagenous protein removal must be performed. Salts and alkali can be added to solubilise non-collagenous proteins. It is important to note that collagen proteins will not be degraded with this step as collagen in comparison with other proteins found in a collagenous sample is significantly more chemically robust and resistant. The Table 4.5 lists the literature recommended chemicals utilised in the removal of non-collagenous protein.

Collagen extraction methodologies vary source to source. This includes major variations such as bovine hide samples requiring hair removing steps to aquatic sources moving to sizing steps at first instance and certain enzymes not having an effect on the cross-linking of mature tissue to slight variations, such as changing the concentration of a salt or an enzyme (O'Sullivan et al. 2006). Collagen extraction literature presents numerous methodologies of extraction, and some of these methodologies have worked better for some tissues over others. Optimisation of collagen extraction is required to reduce costs and to gain a positive environmental impact. Literature analysis has shown seven main collagen extraction methodologies which are outlined in the subsections below.

4.3.7 Salting-Out Extraction

The salting-out method is more historic method of collagen extraction, and it is perceived to be the least favourable method for extracting collagen. Similar to a number of proteins, collagen to a certain extent has the characteristic of being soluble in salt. The concentration of salt required and its ability to break the strong covalent bonds of tropocollagen units is disputed. Low salt concentrations will not influence the cross-links of tropocollagen units, and optimisation of salt concentration for solubilisation of collagen is an area of research that needs to be further investigated.

Table 4.5 Removal of non-collagenous protein—recommended chemicals found in the literature

Collagen source	Recommended chemical	References
Bovine	0.5 M sodium chloride	Fukuta et al. (1998)
	1 M sodium chloride	McClain (1977)
	$K_2HPO_4^-$	Gross et al. (1955)
	0.1 M sodium chloride	Ran and Wang (2014)
Fish	0.1 M sodium chloride	Nagai and Suzuki (2000), Sadowska et al. (2003), Tylingo et al. (2016), Muralidharan et al. (2013), Kiew and Mashitah (2013)

Specifically for mature and thick tissues such as collagen from bovine hides, the salting-out method will not have a significant impact on solubilising the collagen and therefore is not an efficient method of collagen extraction for mature and heavily cross-linked tissues (Yang and Shu 2014).

4.3.8 Alkali-Treated Sample Methods

Comparable to the salting-out method of collagen extract, the alkali method is also not preferred. Historically, the alkali method of collagen extraction required the use of monomethylamine and sodium hydroxide (Hattori et al. 1999). The alkali method of extraction alone is not an effective method of collagen extraction for similar reasons to the salting-out method of extraction; however, some literature states the attainment of similar results to extraction by acid and enzymatic methods. Hattori et al. (Hattori et al. 1999), for example, utilised sodium hydroxide in combination with monomethylamine for extraction of collagen from bovine hides and compared this to extraction with acid and enzymatic methods and concluded that all extracted collagen contained similar content of hydroxyproline.

4.3.9 Alkali and Enzyme Method

This method is more effective than the sole alkali method; however, unlike acids, the alkali does not have the ability to disrupt the tropocollagen units. Its effectiveness can be measured against the acid-enzyme method, whereas acids such as acetic acid can initially fully disrupt the collagen molecule and allow the enzymes to cleave the covalent bonds and release the collagen strands. The alkali-enzyme method can be more effective and cost-effective for production of gelatine (Yang and Shu 2014).

4.3.10 Alkali-Acid Extraction

Repetitive soaking of collagenous tissue in acid and alkali solutions can be applied to retrieve collagen. However, this is an ineffective method as the soaking of the collagenous tissue needs to be prolonged due to slow reaction time and can take days to attain a small yield of collagen. Similar to the salting-out method, the alkali method and the alkali-enzyme method, this method is not effective for mature tissue collagen extraction. This is due to the alkali and acid's inability to disrupt the cross-links found in mature tissues.

There are variances shown in the literature regarding the yield of collagen attained with the alkali-acid method of extraction. The variations in yield could be due to a number of factors including the age of the tissue utilised, the pretreatment

parameters, the temperatures of extraction and the general handling of the collagenous tissue.

Literature has shown that acid types, acid concentration and reaction times influence the overall yield of collagen extracted. The common acids used in conjunction with alkalis in the acid-alkali method of collagen extraction include the use of hydrochloric acid, citric acid and acetic acid. Some researchers have reported that the length of acid solubilisation results in attaining a higher yield of collagen in comparison with shorter periods of acid solubilisation, for example, Skierka (Skierka and Sadowska 2007) studied the effect of acid solubilisation time on yield of collagen extracted, and the study concluded that 72 h of acid solubilisation resulted in approximately 60% collagen, whereas 24 h of acid solubilisation resulted in approximately 33% of collagen.

4.3.11 Acid Solubilisation of Collagen

Weak concentrations of acids such as hydrochloric acid, citric acid and acetic acid are utilised in the acid-solubilisation method to extract collagen (Table 4.6). The concentration of acid has an influence on the extracted yield of collagen; however, low-concentration acids of pH 2–3 are also able to solubilise collagen. Higher concentration of acid is required for more mature collagen-containing tissues. Acids can solubilise collagen via swelling up collagen and further disrupting the electrostatic interactions amongst the tropocollagen units. A number of different acids can be used for acid solubilisation, and different acids may have a different influence on the electrostatic forces of the tropocollagen units; therefore, it is important to work towards optimising methodologies to understand why these acids result in a different collagen yield. Yang and Shu (2014) extracted collagen using acid solubilisation and compared acetic acid and citric acid with hydrochloric acid and concluded that citric acid resulted in the greatest collagen yield. Skierka and Sadowska (2007) and Higham (2010) concluded that acetic acid had the greatest potential to solubilise collagen, while hydrochloric acid was the least effective

Table 4.6 Acids utilised for acid solubilisation of collagen

Collagen source	Acid	References
Bovine	0.5 M Acetic acid	Gómez et al. (2012), Rizk and Mostafa (2016), Mu et al. (2007), Komsa-Penkova et al. (1996), Hattori et al. (1999), Mocan et al. (2011), Park et al. (2012)
	10% Acetic acid with 0.2% hydrochlorhydric acid	Rodrigues et al. (2003)
Fish	0.5 M Acetic acid	Zhang et al. (2007), Tylingo et al. (2016), Chen et al. (2015), Kittiphattanabawon et al. (2005), Park et al. (2012)
	0.15 M HCl	
	Citric acid	Sadowska et al. (2003), Skierka and Sadowska (2007)

solvent. These discrepancies in literature could be due to other variables present in the process, such as the concentration of acid used, the period of solubilisation, the processing temperature, pretreatment of the collagenous tissue and other unconsidered variables.

Disadvantages of applying the acid-solubilisation method of collagen is extraction is that acids can be corrosive and can cause damage to experimental equipment, specifically at large-scale extraction facilities. The addition of an enzyme with low concentrations of acids can prevent the immediate corrosive damage to equipment, and the enzyme enables a faster reaction time.

4.3.12 The Enzyme Method

Majority of collagen researchers have found the enzyme method of extraction to be the most effective and the preferred method of collagen extraction (Table 4.7). The most used enzyme in this space is pepsin; however, papain and tryptase are also used by some researchers (Yang and Shu 2014). At a molecular level, the enzyme of choice used for extraction works by acting on the non-helical parts of the peptide chains that form the collagen protein. The non-helical regions of the peptide chains are the amino telopeptides of the tropocollagen unit, and once the enzyme cleaves the amino telopeptides, the disruption of the cross-linking has occurred. The enzyme cannot cleave the helical regions of the tropocollagen unit, and therefore the recovered collagen is stable and in its native form.

The enzyme method is preferred over other methods of collagen extraction due to the enzyme's selectivity and the preservation of the triple helix. Therefore, collagen extracted using enzymes is preferred due to its chemical stability, purity and high market value. Contrary the acid-solubilisation method, the enzyme method is not harsh or corrosive to production equipment, and due to its specificity and selectivity of cleaving the non-helical regions of the peptide chain, the reaction time is also reduced resulting in a more efficient process (Munasinghe et al. 2014).

For mature collagenous tissue, enzyme solubilisation is preferred. The number of cross-linking increases as the tissue matures and can be insoluble in all acids. The increase of cross-linking with age form keto-imines which are difficult to disrupt and the only way to disrupt these strong intermolecular bonds are to introduce an enzyme

Table 4.7 Collagen enzyme solubilisation found in the literature

Collagen source	Enzyme	References
Bovine	1% (w/w) Trypsin	Kopp et al. (1990)
	Pepsin	Komsa-Penkova et al. (1996), Mocan et al. (2011), Rodrigues et al. (2003), Park et al. (2012)
Fish	1% (w/w) Pepsin	Zhang et al. (2007), Chen et al. (2015), Park et al. (2012)

that cleaves the tropocollagen unit in the specific regions without bringing a change to the purity of collagen. The only disadvantage of enzyme solubilisation is that the enzyme might cleave other proteins too, which may result in contaminated collagen.

Collagen extraction with enzyme solubilisation is often applied in conjunction with the addition of a weak acid.

4.3.13 Acid-Enzyme Solubilisation

The method of acid-enzyme solubilisation is regarded as the most efficient method of collagen extraction. The acid acts to swell the collagenous tissue, while the enzyme acts to cleave the non-helical regions of the tropocollagen molecule enabling the collagen to be soluble in the acid-enzyme solution. The advantages of this extraction method include reduced reaction time, better selectivity and preservation of the triple helix; however, the acids can still be corrosive to the extraction equipment, and enzymes can be expensive. The concentration of the enzyme and the acid utilised in the acid-enzyme solubilisation method of extraction depends on the tissue type and age.

4.4 Biomaterials and Applications of Collagen Derived from Bovine Waste

4.4.1 Collagen-Derived Films

Biodegradable films are transparent and flexible materials that can be derived biomaterials found in nature. Biodegradable films can be derived from starch, whey proteins, collagen and many more renewable polymers (Fairley et al. 1996; Paschoalick et al. 2003). There has been increased interest in the development and use of biodegradable films due to environmental concerns. The packaging industry, specifically the drug and food packaging industry, consumes an immense amount of petroleum-based plastics which can easily be replaced by packaging derived from renewable and natural resources (Cao et al. 2009).

Biodegradable films have several advantages over petroleum-based plastics and films. Some advantages of biopolymer films over synthetic films for the packaging industry include biodegradability, recyclability and the availability of the raw material as it is renewable and found in nature. Biopolymer films have the disadvantage of being inextensible and can have a shorter shelf life in comparison with synthetic films. The extensibility of the biopolymer films can be enhanced by addition of plasticisers. However, plasticisers are known to decrease the tensile strength and stiffness of materials upon addition. To achieve reasonable elongation without tensile strength reduction, research needs to be carried out to identify

plasticisers to use and the concentrations to apply without bringing a negative impact to the overall film properties.

Biopolymer films and coatings, including edible films, fall under the classification of packaging materials. Edible films are a variant of regular biopolymer films in the sense that they are derived from safe and edible ingredients. Biopolymer-derived films can decrease the mass portion of synthetic packaging utilised in the food industry by reducing at least one layer of packaging from a multilayered packaging system. Edible films, comparable to any other biopolymer films, need to hinder the movement of carbon dioxide, oxygen and moisture. In the food industry, edible films as packaging materials are also useful for separation of different units in multiunit foods. Research has shown that edible films in multicomponent food conserve food quality by prohibiting aroma and moisture uptake or loss after the synthetic packaging component of the multicomponent food has been broken.

Similar to packaging films being utilised in any other industry, biopolymer films being utilised in the food industry need to have the characteristics of transparency, advantageous tensile strength and elongation at break, and the films should prohibit the update and loss of aroma and moisture to retain the food quality. Nevertheless, these characteristics would be variant and dependent on the application within the food industry packaging systems.

A possible collagen-derived product is collagen films. Collagen films can have a variety of different applications depending on the innovative engineering applied. One of the commonly applied applications of the collagen films is as coatings or as a packaging material in the food industry.

Collagen has the property of biodegradability, and it is a safe and a nontoxic polymer with great tensile strength; therefore, it has been utilised in the formation of films and coatings in the food industry (Miller 1983). The food industry utilises over 13 million tonnes of plastic per year which contributes drastically to the problem of global warming; therefore, alternative means of packaging need to be investigated. Collagen-based films can act as such alternative. Collagen-based films offer great tensile strength and have the properties of biodegradability and renewability.

Collagen-based films also find use in the biomedical industry. High-grade collagen-based films are utilised as a barrier membrane and utilised for drug delivery and for treatment of infection, namely, for the treatment of diseased corneal tissue (Lee et al. 2001).

Sionkowska et al. (2016) and many other researchers have prepared collagen-based films; in this case, a blend of collagen with silk fibroin was solution casted to prepare biopolymer films. The blend films showed great tensile strength, which is better in comparison with pure silk fibroin films. It was concluded that the better tensile strength in the blend films was due to the great tensile strength of collagen and simultaneously due to the strong molecular interactions between silk fibroin and collagen. The elongation at break of these films was very low, at 0.30–5.10%, and this was given as the blend films were not plasticised. The addition of a plasticiser enables better elongation of the films; however, the addition of plasticisers, specifically at high concentrations, can greatly reduce the tensile strength of the films.

Noorzai et al. (2020) prepared films with extracted collagen from various bovine hides. The collagen-based films showed to have great tensile strength; however, the elongation at break values was very low prior to adding the plasticisers. Post optimisation of plasticiser addition, the collagen-based films showed improved elongation at break values without compromising the tensile strength of the films to a great extent.

It is important to note that the method of collagen extraction has an influence on the ability to prepare films from that extracted collagen. The amount of acid, alkali and enzyme used in the processing of collagenous tissue influences the extracted collagen and, hence, the film formability of that collagen. O'Sullivan et al. (2006), for example, extracted collagen via hydrochloric acid solubilisation and through acetic acid solubilisation. The collagen extracted with hydrochloric acid was not favourable for preparation of films; however, the collagen extracted with acetic acid resulted in smooth and transparent films.

4.4.2 Collagen-Derived Sponges

Collagen-derived sponges are utilised in the biomedical sector for several applications. Collagen sponges find use mainly as a biological absorbance material; however, these sponges are used in the therapy of burns and as dressing for donor sites, pressure sores and other similar cuts and injuries. Collagen sponges have been a success in the medical sector due to their biocompatibility and their ability to take up substantial portion of tissue exudate and simultaneously protect the diseased tissue from physical and bacterial harm (Geiger et al. 2003).

Similar to collagen-based films, collagen sponges have been utilised as vehicle for drug delivery. Lee et al. (2001), for example, have successfully utilised collagen sponges for delivery of antibiotics.

Luo et al. (2019) prepared collagen-based sponges for medical therapy applications. Their findings confirmed the presence of collagen type I with its complete triple helical structure, while simultaneously the collagen sponge possesses a permeable formation with exceptional haemostatic functionality. Nevertheless, the collagen sponge demonstrated weak tensile strength. While the tensile strength of the collagen sponge can be increased via various additives, it is not necessarily an important factor in biomedical applications.

4.4.3 Collagen-Derived Corneal Shields

Collagen-derived shields are thin, transparent and permeable materials which are utilised in the ophthalmic industry. Like the collagen-derived sponges, the collagen shields are used as vehicles of drug delivery for ocular disease treatment. The collagen-derived corneal shields have been utilised for delivery of medications to

the eye, and this includes medications that are antiviral and antifungal. The collagen corneal shields protect the eye from physical and bacterial harm while aiding the healing of the ocular tissue (Willoughby et al. 2002).

Collagen corneal shields have been proven to be effective in the ocular drug delivery space in comparison with traditional methods. The noninvasive feature of collagen corneal drug delivery has enabled this method of ocular drug delivery to be the most widely adapted and preferred method. More research needs to be carried out in this space for slow-release drug delivery and to treat other vision-threatening diseases.

The collagen utilised for preparation of corneal shields needs to be of medical grade, and hence the extraction method utilised for recovery of collagen needs to be carefully monitored to prevent collagen denaturation and contamination.

4.4.4 Collagen for Skin Replacement and as Bone Substitutes

Collagen-based bandages, sponges and sheets and scaffolds have been utilised for treatment of wounds, diseases and injuries (Wisser and Steffes 2003). However, collagen utilised for medical purposes such as for replacement of skin need of a specific type of collagen. Collagen type I is desirable for preparation of collagen sponges and for replacement of skin due to their superior tensile strength and nontoxicity (Meena et al. 1999). Collagen has been utilised in medical therapies, for example, as implanted vehicles for bone-generating proteins (Geiger et al. 2003), as bone substitutes (Lee et al. 2001) and as scaffolds for orthopaedic defeats.

4.4.5 Collagen in 3D Printing Applications

The process of converting computer-aided design (CAD) imagery to tangible and physical objects is referred to as three-dimensional (3D) printing. An object of interest is designed on CAD, and the designed object is separated into cross sections enabling the 3D printer to construct the desired object in a stratified fashion. A 3D printer can utilise almost any material to construct a physical object. Recently, several biomaterials have been applied in 3D printing for a number of different applications and industries; these include the use of plastics, paper and metals (Petronzio 2013). Bioprinting, on the other hand, is the process of 3D printing with cell-laden biological materials such as collagen (Funk 2013).

There are several different bioprinters available in the market, and printing mechanisms vary and depend on the type of printer. Similar to other 3D printers, bioprinters function by layer-by-layer deposition of material of interest via the bioprinter nozzle to create a physical product.

Worldwide, there is a shortage of organs required for replacement surgeries. The waiting lists for kidney transplant, heart transplants and liver transplants are

increasing yearly, and in the United States, over 100,000 people are currently on waiting lists for kidney transplants. This a worldwide problem that needs to be addressed in a renewable manner. The increase of life expectancy and shortage of organs required for replacement surgeries require alternative methods of problem-solving. Recent research has shown indications of utilising bioprinters to print living systems. Bioprinters with the aid of scaffolding materials such as collagen can enable to printing of living organs. Researchers at Cornell University attempted at printing the human ear. Pictures of a child's ear were taken with a 3D camera and mirrored into printing a model of the human ear. The bioprinter in this case was laden with cartilage cells from ears of cows, and collagen was utilised as the base or the vehicle to act as the scaffold post printing (Reiffel et al. 2013). Scientists at Wake Forest Institute utilised bioprinters to print kidneys. Collagen was injected with kidney cells, and the prototype kidney was printed in a stratified manner (Mironov et al. 2007). Bioprinting of skin tissue has also been investigated by several researchers.

4.4.6 Collagen in Cosmetics

Collagen is a major component of skin giving skin structure and integrity. Mature skin becomes wrinkled and weak due to loss of collagen. Collagen often is referred to as the "restructuring" protein in the cosmetic industry as collagen is found through the healing of skin post-injury. The great tensile strength and biocompatibility of collagen make it an ideal ingredient in cosmetics. Collagen has been utilised in both skin and hair cosmetic formulations. Out of the approximately 27 types of collagens, type III collagen is prevalent in young tissues. The increase in the world's age expectancy and the demand in young-looking skin have led researchers to include collagen in creams and cosmetic injections in effective approaches.

Collagen from several different sources can be utilised for cosmetic applications; however, bovine collagen is the most preferred collagen source. Collagen extracted from fish, porcine and other cattle has been utilised in cosmetic creams and injections. Collagen from different sources has unique biochemical properties, including distinct thermal stabilities. Hence, research needs to be carried out to understand which source results in collagen that can be effective in cosmetics and further not to have a detrimental effect on the shelf life of the cosmetic creams and injections.

4.5 Conclusions

Researchers, scientists and governments have realised the need for ecologically sound methods of waste disposal and treatment. Simultaneously, there is an increasing demand for biodegradable, renewable and economically friendly materials in all industries. The agricultural industry produces tonnes of waste and by-products that

have the potential to be processed to produce high-value and environmentally friendly materials. The processing of agricultural industry waste, specifically from the leather manufacturing, needs to be managed in sustainable methods to reduce further negative impact on the climate. Sustainable waste valorisation techniques can be applied to derive high-value products from the leather manufacturing industry. A component of the attempts to improve the valorisation of agricultural by-products, researchers have developed methodologies to improve collagen extraction from agricultural waste and to apply this high-value protein in several life-changing applications.

Collagen has increased its position to be an essential raw material and as a component of importance in several industries, including the medical and nonmedical sectors. Applying theories of waste valorisation, collagen from cattle hides and other collagen-containing agricultural waste can be extracted in an efficient manner. Collagen from waste agricultural by-products has the potential to be an alternate source of collagen to be utilised in a myriad of applications.

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Chapter 5
Valorization of Agricultural Lignocellulosic Plant Byproducts Following Biorefinery Approach Toward Circular Bioeconomy

A. C. Cassoni, R. Gómez-García, and M. Pintado

Abstract During the last decade, an increased attention has emerged on circular economy focused to improve simultaneously the environment, economy, and society for a sustainable development. In this context, biorefinery systems act as tactical mechanisms for the transition of a circular bioeconomy, since these systems can produce multiple high-value products, among biofuels, including food and feed products, biochemicals, and biomaterials, coming from diverse biomasses through the integration of useful conversion technologies. Agricultural activities are responsible for the overaccumulation and overproduction of lignocellulosic waste (e.g., bagasse, branch, leaves, wheat stover, fruit and vegetable seeds and peels). Such waste biomasses are abundant and could be considered as versatile natural resources for the obtention of this kind of products with high industrial demand. Thus, exploiting these lignocellulosic materials for the obtention of bioenergy and biochemicals, among other products, under biorefinery approach is a key objective for the transition of a well-succeeded circular bioeconomy. In this chapter, we focus on the principal constituents such as cellulose, hemicellulose, and lignin present in the lignocellulosic biomasses. Each component has its unique characteristics, and their valorization depends on effective biomass treatment. This chapter presents traditional and novel treatment methods for agricultural lignocellulosic biomass valorization and their potential applications.

Keywords Agricultural waste · Lignocellulosic biomass · Biorefinery approach · Circular bioeconomy · Novel technologies · Industrial demand

A. C. Cassoni and R. Gomez-García contributed equally with all other contributors.

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5.1 Introduction

Presently, worldwide agricultural lignocellulosic biomass generation means environmental pollution and loss of treasured renewable materials that can be converted into value-added goods for industrial purposes (Yusuf 2017). At present, agricultural activities produce closely 1000 million tons of agricultural biomass per year, which later become wastes due to the lack of efficient management strategies and scarcity of effective eco-technologies for their integral valorization (Periyasamy et al. 2022). The null exploitation of these debris produces environmental issues related to the emission of toxic fumes, principally sulfur and carbon dioxide, as well as pollution of subterranean water (Blahuskova et al. 2019). The lignocellulosic materials are comprised mainly of three types of natural biopolymers, which are toughly joined and chemically connected by non-covalent and covalent cross-linkages: cellulose with the highest percentage (30–50%), followed by hemicellulose with the second largest amount (15–35%) and lignin with the lowest content (10–20%), although this parameter can vary depending on the sources (e.g., wood 30–40%) and some minor components, also known as extractives (4–6%), characterized as proteins, lipids, and minerals (Bilal et al. 2017).

On the other hand, lignocellulosic waste valorization under zero-waste approach could promote circular bioeconomy and highlight them as novel renewable resources, reducing the need on products derived from petroleum and enhancing waste management strategies following the European Directives for reusing and recycling waste materials (Esparza et al. 2020; Gómez-García et al. 2021a, b). Over time, different traditional technologies have been used to convert agricultural biomasses and produce new different products. Traditional technologies can be divided into mechanical (milling, separation, drying, and pelletizing), chemical (alkali-acid hydrolysis, supercritical and solvent extraction), and thermochemical (pyrolysis, gasification, hydrothermal liquefaction, and combustion) processes (Ruiz et al. 2011; Negro et al. 2017; Atelge et al. 2020). Although these technological processes have shown the ability to produce important final products such as simple sugar (among other products) for bioethanol conversion as principal revenue stream, they remain infeasible and exhibit a need for further cost reductions and environmental efficiency. In this regard, diverse novel/green technologies have gained special attention as cheaper as well as more suitable and environmentally friendly processes to exploit lignocellulosic waste such in the case of nonthermal processes (surface-active ionic liquids [ILs] and deep eutectic solvents, DES) and biological treatment (fungi fermentation, anaerobic digestion, and enzymatic hydrolysis) (Ren et al. 2015a, b; Karnaouri et al. 2019; Chen and Lahaye 2021; Vaz et al. 2022).

Bioeconomy is prompting the implementation of biorefinery approach within the industrial value chain, which expands the production streams of a treatment platform, generating diverse products together with biofuels with the aim to increment revenue streams (Gavrilescu 2014; Tsegaye et al. 2021). Biorefinery systems are defined as a cascading process to manufacture various commodities (products) from one or more raw materials (e.g., lignocellulosic waste) by the integration or

combination of different (traditional or novel) technologies, allowing a complete exploitation of these wastes to produce biochemicals, biomaterials, biofuels, bioenergy, foods, feed and goods, serveries, and possible jobs (Fig. 5.1) (Imbert 2017; Campos et al. 2020). In the last decade, biorefinery systems are considered vital high points as the greatest and most appropriate opportunity to convert different biomasses into a wide array of valuable products (Katakojwala and Mohan 2021). For example, these systems can produce multiple products such as proteins for human consumption (food and feed), bioethanol and biogas (biofuels), fertilizers, antioxidants, sorbitol (biochemicals), hydroxybutyrate, adhesives, and composites (biomaterials), among others (Dahiya et al. 2018; Solarte-Toro et al. 2021). Furthermore, the biorefinery concept can be entirely integrated with well-established biotechnological developments such as digestion by anaerobiosis, which can make bioenergy and fertilizer employing the same bioprocess. Moreover, within the biorefinery concept is included the management of sustainability issues related to environmental, economic, and social sectors, assuring an efficient strategy focused on the green era to support economic growth and sustainable development (Liu et al. 2021; Vance et al. 2022). All these areas are global trends in a very straight connection with the European policies within the framework of plant-based products, green technologies, and market innovations that all together will contribute to mitigate the environmental issues and comply with the social and industrial demands (Sindhu et al. 2019; Kumar et al. 2021).

Therefore, this chapter summarizes the key technological processes that have been employed for lignocellulosic waste valorization, focusing on various novel technologies and their integration in biorefinery systems for circular bioeconomy development by producing different high-demand bioproducts.

5.2 Lignocellulosic Biomass Composition

Lignocellulosic plant waste is categorized as the leftovers and byproducts arising from agricultural activities (farming, pruning, harvest) and the processing of farm products (crops, vegetables, and fruits) such as branches, leaves, bagasse, noncompliant fruit, peels, and seeds. One similarity between these wastes is that the main component is cellulose, continued by hemicellulose and lignin, and in less extend extractives (proteins, lipids, and minerals) (Sluiter et al. 2008; Gómez-García et al. 2021a, b). Cellulose and hemicellulose are macropolymers constituted of different sugars, while lignin is an aromatic polymer synthesized from phenylpropanoid precursors (Fig. 5.2).

5.2.1 Cellulose

Cellulose known as a linear natural polymer is composed of D-glucose monomers linked by β-1,4-glycosidic linkages constructing cellobiose dimer, which in turn

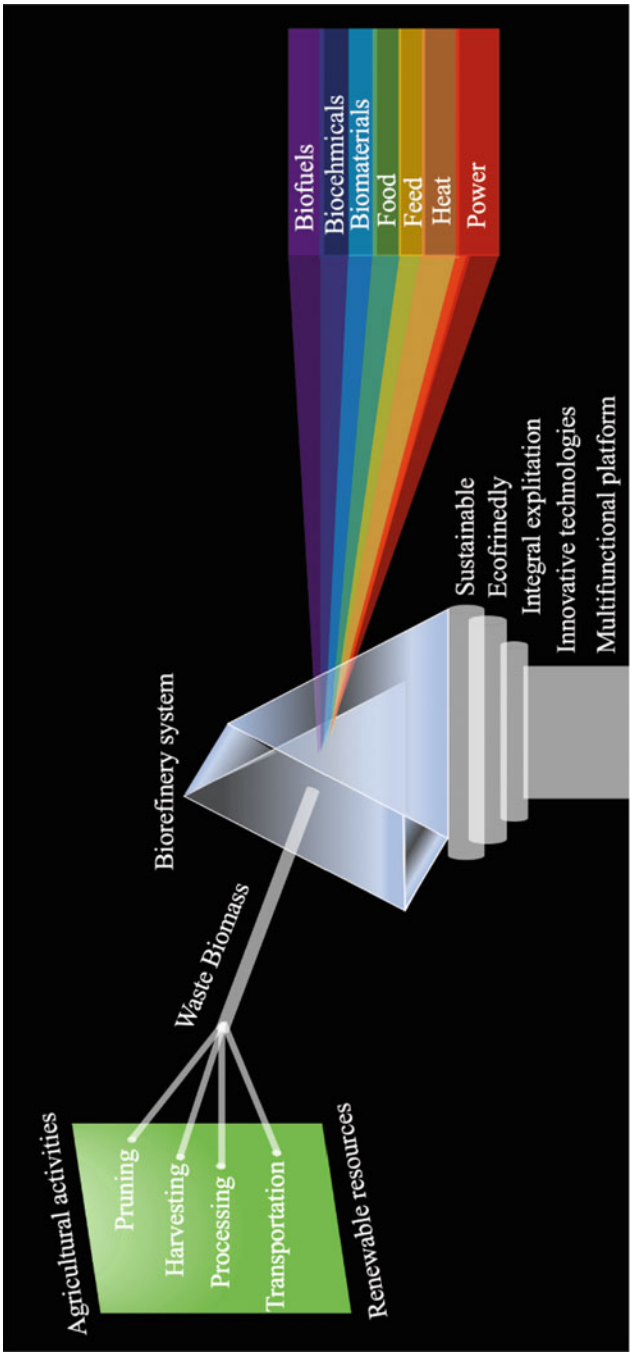

Fig. 5.1 Graphical representation of biomass processing through biorefinery approach, its features, and value-added bioproduct obtention. (Reprinted with permission from Gavrilescu (2014))

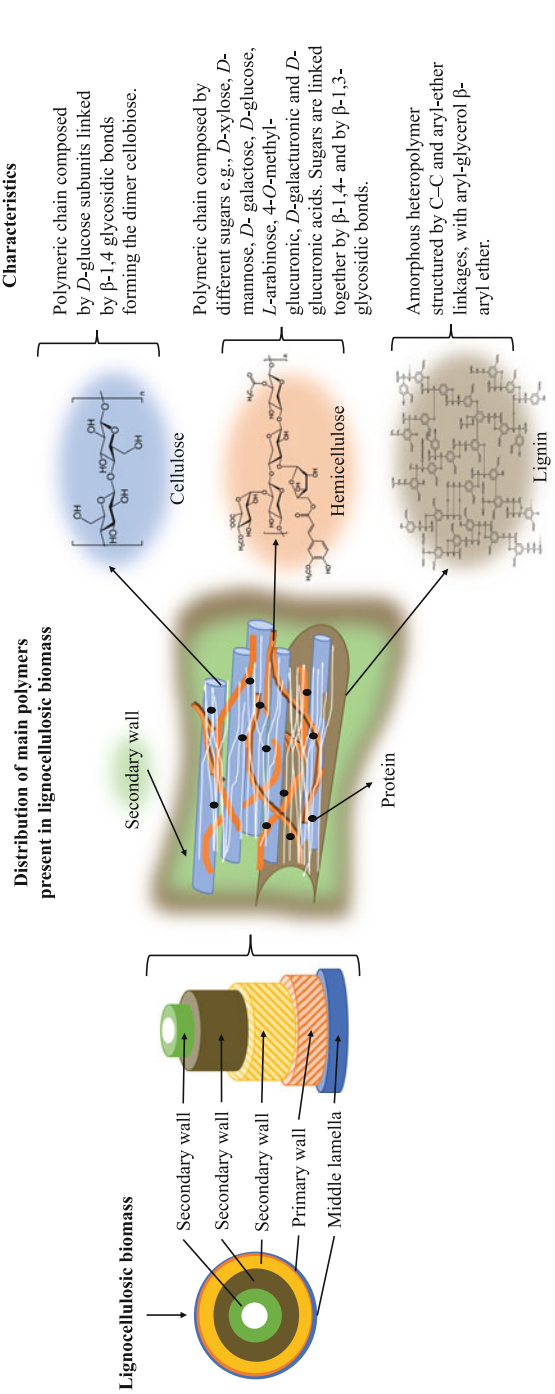

Fig. 5.2 Graphical representation of lignocellulosic biomass structure and composition. (Adapted from Bilal et al. (2017) and Gómez-García et al. (2021a, b))

forms long fibrils connected by hydrogen bonds and van der Waals forces (Naduparambath and Purushothaman 2016; Zhao et al. 2018). Cellulose properties depend on its chain length or the degree of polymerization and the total number of glucose units that make up the homopolymer chain. This natural polymer is generally found in a mixture of hemicelluloses, lignin, and other molecules. In biosynthesis, cellulose subunits are grouped forming microfibrils and are packed into microfibrils comprising amorphous and crystalline zones (Haldar and Purkait 2020).

Cellulose polymer is recognized by its hydrophilicity, low density, and reinforcing ability. Additionally, it has environmental benefits and has interested numerous industries to work on developing materials or composites constituted by cellulose (Rajinipriya et al. 2018). Cellulose can be hydrolyzed applying strong acids or enzymes to remove the amorphous regions. After cellulose hydrolysis and based on the range of elimination of the amorphous zones and on the lengths, microcrystalline (MCC) and nanocelluloses can be made. The MCC is a white crystalline powder, also known by its null toxicity, biodegradability, biocompatibility, mechanical strength, great surface zone, and very little density, and it has involved huge considerations throughout the last 20 years (Kuhad et al. 2016). For example, it was applied as a binder and filler in food and medicinal pills and exceptionally as support agent in the elaboration of composites. Moreover, MCC was employed as a stabilizer, a water retainer, a viscosity regulator, and emulsifier in food products (pastes and creams). The cellulose-based products and its derivatives have been used for a broad range of purposes such as food additives, paper manufacturing, pharmaceuticals, or other chemical engineering use such as chromatography, paints, and explosives (Ni et al. 2018; Vallejo et al. 2021).

Agro-industrial byproducts could be promising and important resources of cellulose polymer that, after its isolation and extraction, could be used instead of the petroleum derivatives (plastics) as reinforcement products for building construction materials and fillers in biodegradable composite, packaging, and agriculture, which are in terms of biodegradability more accepted for environment protection and preferable for a sustainable modern lifestyle.

5.2.1.1 Traditional Pretreatment Techniques

To date, many significant treatments have been carried out to convert lignocellulosic waste to value-added products, comprising composite, chemicals, animal feed, paper, biofuels, and enzymes (Ren et al. 2015a, b). The most decisive phase for an effective employment of lignocellulosic biomass is delignification, which rushes the isolation of the principal biomass constituents (cellulose and hemicellulose) (Rabelo et al. 2011). In this regard, the conversion is blocked due to the high complexity of the biomasses structure, making these materials a challenge for their total exploitation. Traditional processes involved in the lignocellulosic biomass conversion include physical disruption (FD), chemical hydrolysis (CH), and thermochemical treatments (TCHTs); although these processes are consolidated strategies and have been broadly explored throughout many years by researchers and some industries,

several of them are presently categorized as non-sustainable nor environmentally friendly processes, and therefore away to comply with the new policies (Bilal et al. 2017; Periyasamy et al. 2022).

Milling (disk, ball, hammer, two-roll, and colloid milling) is a well-known FD technique that mechanically crushes the particle size of biomass from macro- (m or cm) to microscale (μm), improving particle control throughout the handling steps by increasing bulk density and surface area-to-volume ratio. The main disadvantage of this technique is the huge energy needed, which raises the capital charge and investment, operating expenses, scale-up risk, and equipment damage (Postma et al. 2017).

Acidic (H_2SO_4, HCl, and H_3PO_4) and alkaline (NaOH, KOH, and NH_4OH) treatments are CH methods. Both chemicals help with the hydrolysis of biomass and the solubilization/hydrolysis of lignin (Patel et al. 2019). These reactions improve the cellulose content used to make value-added products. Acidic pretreatment can be prepared with either a concentrated acid at low temperatures (30–60 °C) or diluted acid at high temperatures (120–210 °C), and alkali also can work at low temperatures (30–60 °C). However, both methods have some serious issues, including toxicity, equipment damage, and the production of hazardous compounds (furan, furfural, and derivatives) as well as negative aspects related to long times of hydrolysis from hours to days and the need to neutralize the wastewater streams (Rajinipriya et al. 2018).

Steam explosion is one of the most successful TCHTs applied at small and large scale. The biomass is subjected to high-pressure saturated steam for short times, and the pressure is purged quickly. In the steam explosion, biomass is heated at high temperatures around 150–300 °C and starting pressure of 20–50 bar for a few minutes (Boluda-Aguilar et al. 2010). This process dislocates the cell wall structure and removes hemicellulose and lignin by solubilization, and then cellulose fibers became more available. Additionally, this technique allows the development of crystals in the amorphous region of cellulose, increasing its crystallinity index. However, the lignin-carbohydrate structure can be degraded, which rises the condensation and precipitation of soluble lignin materials, formulating biomass less digestible. Normally, inhibitor products from fermentation are produced at upper temperatures, which reduce saccharification yield by 20–25% because of the eliminating soluble molecules (Ren et al. 2015a, b).

5.2.1.2 Novel/Emerging Pretreatment Techniques

Microwave is an emerging FD technique, employing radiation frequency (300 MHz–300 GHz). Microwave radiation is a pretreatment method in which the biomass absorbs radiation, and the particles are agitated to a superior energy level, breaking the chemical linkages between carbohydrates (Kumar et al. 2021). The electric field of microwaves changes their energy to the molecules, developing a thermal energy. Microwave irradiation modifies the structure of cellulose, moderately eliminates hemicellulose and lignin, and disturbs the surface conformed by

waxes. The advantages of microwave irradiation are (1) low energy consumption, (2) superior uniformity and selectivity, and (3) shorter residence times (Lucas-Torres et al. 2016).

Pretreatment by ILs is a CH process, better and economically viable technique than the acidic and alkaline methods. The application of this technique involves a little quantity of ILs to split lignocellulosic biomass components (Martins et al. 2021). The vapor pressures of ILs are low, making this process suitable for its application with less economic impact and safety method. Additionally, IL pretreatment technique can dissolve carbohydrates and lignin both together. ILs are organic salts with a lower melting temperature ($\geq$100 °C), containing cations and anions (Almeida et al. 2014). The central characters disturbing the relationship among the ILs and the lignocellulosic biomasses during the pretreatment are cations, anions, time, and temperature. The IL pretreatment has different benefits such as mild operation conditions, economical, environmentally friendly, easy to reuse, usage of less harmful reagents, and superior thermal and chemical stability (Vaz et al. 2022).

Ammonia expansion is a TCHT used for cellulosic biomass treatment that uses ammonia (NH_3) as the key reactant. The processing of biomass with ammonia explosion is carried out with ammonia in liquid form and the steam explosion fundament. The process works at very elevated pressure (1.72–2.06 Mpa) and slightly elevated temperature (60–120 °C) during 30 min with the discharge of pressure (Periyasamy et al. 2022). In this technique, the biomass is subjected with liquid ammonia under pressure environments and heated to optimal temperature. Once the optimal temperature is reached in the system, the rapid expansion of ammonia gas conducts to the breakdown of the complex lignin polymer, thereby improving the digestibility. This technique brings some benefits when compared with the steam explosion: (1) soft procedure conditions (temperature $\geq$ 100 °C), short reaction time, (2) capability to recover and recycle ammonia, (3) higher selectivity for reaction with lignin, and (4) viable and continuous method (John et al. 2017a).

Another technology, such as carbon dioxide (CO_2) explosion treatment, is related to ammonia and steam explosion techniques, both TCHTs. This technique is cheaper than the NH_3 explosion, economically and productively/efficiently speaking, and there is no development of inhibitor approaching the steam explosion (Negro et al. 2016). It uses supercritical CO_2 with high pressure to increase lignin cleavage and cellulose accessibility. The CO_2 comes into the biomass at high speed and pressure, and when it is in contact with water, it produces carbonic acid (H_2CO_3), which in turn facilitates the rupture of hemicelluloses. The liberation of the condensed gas produces the disruption of the lignocellulosic structure, increasing the surface area of the target constituent (cellulose). The CO_2 explosion shows several gains, including nontoxicity, nonflammability, particle size reduction, and lower production of residue streams requiring neutralization. Supercritical CO_2 fluids have a liquid-like density, gas-like diffusivity, and viscosity transport characteristics. Also, the fast and noncomplicated exclusion of CO_2 by depressurization does not generate any waste stream, formulating the recapture process cleaner. However, there is still some

limitation of this CO_2 explosion pretreatment related to the expensive and big equipment needed that can resist high-pressure environments of the pretreatment process (Morais et al. 2015).

Enzyme-assisted processes are notable biological conversion techniques for lignocellulosic biomass treatment due to the ability of enzymes to catalyze reactions at temperatures $\geq$90 °C in a wide range of pH values (4–9) (Gómez-García et al. 2021a, b). Enzymes like cellulase, hemicellulase, cellobiase, α-amylase, xylanases, laccases, and lignin peroxidase are the most used biocatalysts to hydrolyze the main components of biomass by the hydrolysis of β-1,4-glycosidic linkages between glucose-glucose bonds (cellulose) and β-1,4-D-glycosidic linkages in xylans present in hemicellulose and oxidation (O_2) of lignin, and others such as proteases, pectinases, pectinesterases, and lipases are also used to enhance the digestion of biomass (John et al. 2017b). One of the key features of this technique is the cell wall disruption, which releases certain phytochemicals (phenolics, pigments, oils) linked to carbohydrates, lipids, and protein chains. Additionally, this process has several benefits such as good conversion rates, high extraction yield, quality of extract, green extraction (nontoxic solvents needed), capability for scaling-up, and reduced purification process (Kumar et al. 2021).

Solid-state fermentation is another biological treatment that is gaining important interest in several industries (pharmaceuticals, food, textile) since it represents a nature-like and eco-friendly process, which is carried out by microorganisms such as fungi (more preferable/studied) and bacteria or yeast (less studied) at mild conditions of temperatures (20–60 °C) and low humidity (50–60%) that allows the hydrolysis of the lignocellulosic structure of biomass (Yoon et al. 2014; Gómez-García et al. 2018). This fermentative process has the advantages associated with higher production yields and low wastewater generation and usage, decreasing the probability of bacterial contamination. In addition, lignocellulosic waste is used as support and carbon substrate for microbial growth. In this way, microorganism can produce extracellularly different enzymes and catalyze the carbohydrate structure of biomass by the same mechanism stated for enzymatic-assisted conversion. Additionally, this technique is categorized as a multipurpose bioprocess with enormous potential for many novel applications for lignocellulosic biomass bioconversion to obtain simple sugars, organic acid, antioxidants, pool of enzymes, and bioremediation agents, among others (Peña-Lucio et al. 2020).

5.2.2 Hemicellulose

Hemicellulose is an abundant polysaccharide (Peng and She 2014), representing 15–30% of lignocellulosic biomass (Kapu and Trajano 2012). It is closely associated with lignin and cellulose through hydrogen and covalent bonds, creating a complex, stable, and resistant structure (Qaseem et al. 2021). Hemicellulose is distinct from cellulose by being smaller, with lower polymerization degree and noncrystalline structure (Ginni et al. 2021; Luo et al. 2019).

It has a primary amorphous and arbitrary structure, composed of four main heteropolymers–xylans, mannans, β-glucans, and xyloglucans (Ginni et al. 2021; Peng and She 2014). D-glucopyranose, D-mannopyranose, D-galactopyranose, L-arabinofuranose, D-xylopyranose, and D-glucuronic acid are the basic glycoelements (Hansen and Plackett 2008). The amount and structure of hemicellulose differ among different plants, with woody biomass having more hemicellulose than agricultural biomass (Vassilev et al. 2012). Additionally, grass species are characterized by having a majority of arabinoxylans, softwood species have mostly acetylated galactoglucomannans, and hardwood species have more *O*-acetyl-4-*O*-methylglucurono-β-D-xylans (Peng and She 2014).

Xylans are comprised of residues of xylose linked by β-(1,4)-linkages (Rennie and Scheller 2014) with phenolic, acetyl, ferulic, and coumaric acids, among other small groups, attached to the backbone. Xyloglucans occur in all types of plants, and its amount varies from 2 to 25% of the cell wall (Hsieh and Harris 2009; Popper and Fry 2003). The backbone of xyloglucan is composed of β-D-glucopyranosyl residues that can be further substituted by short polysaccharides, oligosaccharides, or even mono- or disaccharide chains depending on the plant, tissue, or stages of development (Obel et al. 2009; Schultink et al. 2014). Mannans are involved in the preservation of plant's cell wall structure (Moreira and Filho 2008), and they are divided into four types: homomannans, galactomannans, glucomannans, and galactoglucomannans. Homomannans and galactomannans are composed only of mannose residues linked by β-1,4-linkages. Glucomannans and galactoglucomannans also have a backbone composed of mannose residues but with glucose interruptions (Qaseem et al. 2021). Mixed linkage glucans are more specific to grasses and green plants (Qaseem et al. 2021) and are composed of glucose chains linked by β-1-4 linkages with β-1-3 linkage interruptions (Qaseem et al. 2021).

5.2.2.1 Hemicellulose Extraction

The valorization of hemicellulose from agricultural residues relies on an effective extraction. In fact, the final structure of extracted hemicellulose also varies according to the extraction method (Jin et al. 2019). Physical and chemical pretreatments are the most used, including autohydrolysis, steam explosion, microwave-assisted, ultrasound, alkali, acid, and organosolv (Zhao et al. 2020). However, the extracted hemicellulose has strong hydrogen bonds and poor flexibility which may limit its applications (Lu et al. 2021). Therefore, hemicellulose modification after its extraction from the lignocellulosic biomass is also a crucial step for its valorization (Lu et al. 2021). Standard procedures for modification are etherification, esterification, graft copolymerization, and cross-linking (Lu et al. 2021).

Due to the absence of chemicals, physical methods, autohydrolysis, and steam explosion contribute to environmental pollution reduction. However, they require high energy consumption (Lu et al. 2021). Autohydrolysis is a promising method that selectively dissolves hemicellulose at relatively low temperatures and short

times (Lu et al. 2021; Ma et al. 2012). The resulting hemicellulose usually has a high molecular weight with a wide range of potential applications (Lu et al. 2021). Pretreatment of wheat straw using autohydrolysis enabled 73.65% yield (Yang et al. 2020). A study using corn straw was able to recover 63.2% of solubilized xylan in the form of xylo-oligosaccharides, xylose, and arabinose (Moniz et al. 2013). Steam explosion was performed in corn residues, and yield reached 82% (Makishima et al. 2009). Similarly, it was possible to recover 81.4% hemicellulose from banana rachis (Tiappi Deumaga et al. 2020).

Chemical methods are commonly used due to their efficiency. Alkaline is one of the most applied methods, and it is based on the destruction of the cellulose and lignin bonding to hemicellulose, resulting in high-purity hemicellulose (Lu et al. 2021). Hemicellulose with high purity was successfully extracted from various agricultural residues using NaOH (Braga and Poletto 2020). Recovery of xylan from sorghum bagasse was optimized using also NaOH (Wei et al. 2018). H_2O_2 is also commonly used, and studies on wheat straw recovered hemicellulose with high purity (Azeredo et al. 2015; Pereira et al. 2017). In addition to the high purity, it is also possible to recover hemicellulose with high yield. A method using 6% H_2O_2 recovered 86% hemicellulose with high purity from sugarcane bagasse (Brienzo et al. 2009).

Acid method is based on the breakage of hydrogen bonds between cellulose and hemicellulose (Chotirotsukon et al. 2020). Typically, hemicellulose yield and molecular weight are low (Lu et al. 2021). A study using diluted H_2SO_4 reached a recovery of 78.99% of xylan, mannan, and galactan (Jeong et al. 2010) from rapeseed straw. Pretreatments using solvents comprise organosolv, ILs, and DES. Organosolv extraction allows a hemicellulose recovery with preserved structure, high purity, and good activity, with broad applications. However, the organic solvents may lead to environmental problems due to their toxicity, volatility, etc. (Lu et al. 2021). ILs appear as a greener alternative to organic solvents, allowing solvent recycling (Lu et al. 2021; Mohan et al. 2015). The obtained hemicellulose presents some impurities and is more degraded than organosolv hemicellulose, impairing the possible applications (Lu et al. 2021). Another environmentally friendly method to extract hemicellulose from biomass is through DES, which are easy to prepare and recyclable (Lu et al. 2021). However, hemicellulose purity might be lower due to the simultaneous dissolution of lignin (Lu et al. 2021).

Finally, a combination of methods allows an improvement of hemicellulose recovery but may constrain economic sustainability. For example, ultrasonic technology applied with alkaline extraction improved hemicellulose yield and purity from wheat straw (Sun and Tomkinson 2002). Likewise, it was possible to improve hemicellulose extraction from grape pomace while using a short reaction time and mild temperatures (Minjares-Fuentes et al. 2016). Autohydrolysis is also commonly combined with other methods, as alkaline and acid. Extraction of hemicellulose from corn stalks using a combination of autohydrolysis and alkaline methods yielded almost double when comparing with the yields obtained with each of the methods separately (Lu et al. 2021).

5.2.2.2 Hemicellulose Application

Hemicellulose has the potential to have several applications due to its value-added properties such as biodegradability, biocompatibility, and bioactivity (Peng and She 2014). Moreover, intermediate products produced in the extraction process can also be added to its value. Further modification of obtained hemicellulose and respective intermediate products may increase its potential, improving applicability in several industries such as food, medicine, energy, and polymers (Qaseem et al. 2021).

Hemicelluloses can be directly incorporated in food matrices conferring and improving various properties. Xylans are incorporated into foods acting as dietary fiber and promoting bowel movement (Mudgil and Barak 2013). Xylan incorporation in dough enhanced its properties and bread texture (Ebringerová 2005; Izydorczyk and Biliaderias 1995), and the structure of low-fat yogurts was also improved (Rosa-Sibakov et al. 2016). β-glucans are usually used as fat substitutes in several foods, contributing to the development of low-calorie products (Biliaderis and Izydorczyk 2006; Volikakis et al. 2004). Also, a study showed that the incorporation of β-glucans in snacks improved their glycemic response (Brennan et al. 2013). Xyloglucans have gelling properties and are useful in jams and mayonnaise, among others (Qaseem et al. 2021). It is also being used in dough to improve stability, loaf volume, and storage (Jang et al. 2018; Maeda et al. 2007). Mannans have also several applications such as prebiotic, texture stabilization, dressings, stiffening, etc. (Singh et al. 2018).

Besides applications in food matrices, hemicelluloses are also relevant in food packaging. However, its application depends on modification processes that enhance the mechanical and barrier properties (Zhao et al. 2020). Hemicellulose film was efficient in preserving green peppers compared to traditional cling film (Zhang et al. 2020). A plasticized film based on arabinoxylan and galactoglucomannan was also efficient for long-term preservation (Heikkinen et al. 2014). Combining hemicellulose with other polymers is also being studied for the enhancement of packaging properties (Gao et al. 2018). It is the case of Goksu et al. (2007) that prepared a blend of lignin and xylan. Combining nanofibrillated cellulose with xylan improved the tensile strength and barrier properties (Gordobil et al. 2014; Ren et al. 2015a, b). A blend of locust bean gum with carrageenan and xylan and galactoglucomannan produced a biodegradable film (Ruiz et al. 2013).

In the field of medicine, hemicellulose can be used as an encapsulating agent for the effective delivery of drugs (Souza et al. 2019). In addition, valuable properties for the field are attributed to hemicellulose, such as antimicrobial, antioxidant, antiproliferative, anticoagulant, anti-inflammatory, immune-stimulating, antidiabetic, anti-obesity, and prebiotic properties (Daus and Heinze 2010; Devaraj et al. 2019; Ebringerová and Hromádková 1999).

5.2.3 *Lignin*

Lignin is an aromatic biopolymer with a complex structure (Anwar et al. 2014; Feofilova and Mysyakina 2016) composed of monolignols *p*-coumaryl, coniferyl, and sinapyl alcohols from which derive the primary phenylpropane monomers, *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively (Feofilova and Mysyakina 2016; Kai et al. 2016). Complex C–O–C and C–C interunit linkages bond the monomers, with a ~50% prevalence of β-O-4 linkages (Wang et al. 2019). Lignin is responsible for the rigidity and resistance of plant biomass, being essential to its defense mechanism (Strassberger et al. 2014). Moreover, lignin composition and amount vary according to the type of biomass: grasses are characterized by having a higher amount of H units (5–35%) and 15–25% of lignin; softwood has a predominance of G units and 24–33% of lignin, and hardwood has a similar amount of S and G units and 18–25% of lignin (Abdelaziz et al. 2016; Feofilova and Mysyakina 2016).

Comparing with the carbohydrate fractions of lignocellulosic materials, lignin is still an underrated biopolymer, especially when it comes from agricultural byproducts. Nonetheless, research efforts on agricultural lignin have been increasing in the last years, with a growth of ~500% from 2010 to 2020 (Cassoni et al. 2022a, b).

5.2.3.1 Lignin Extraction Methods

An efficient lignin extraction is key to the valorization of agricultural byproducts. The crops with the most lignin extraction studies are sugarcane, wheat, corn, and rice (Cassoni et al. 2022a, b). These four crops have the highest global production per year (FAO 2020), meaning that a great number of byproducts are being produced, which can justify the higher number of studies on these crops. Nonetheless, agricultural byproducts are extremely diverse, and hardwood species, as well as fruit residues, are less studied concerning lignin. Olive, coconut, vine, and apple are examples of crops with very different natures that are also valuable lignin sources.

There are several methods to extract lignin from biomass. Some are established at an industrial scale, and others are used in the biorefinery context. New emergent and more environmentally friendly methods are also being developed. Lignin extraction frequently involves harsh treatment conditions with negative impacts such as structural damage and chemical modifications (Feofilova and Mysyakina 2016; Wang et al. 2019). Dioxane-water extraction mixture allows a good yield of lignin recovery, and it is suggested to be a model of protolignin (native lignin from the cell wall) (Feofilova and Mysyakina 2016). Milled wood lignin (MLW), the result of grinding plant biomass in a ball mill, is believed to match the native lignin structure but with a low yield (Björkman 1954). This MLW can also be treated with enzymes, resulting in milled wood enzyme lignin (MWEL) that has 95% of lignin but with carbohydrate contamination (Chang et al. 1975). These methods allow for a lignin recovery at laboratory scale and are useful to study the native structure of lignin.

Various authors reviewed methods for lignin extraction established at an industrial scale, namely, kraft, sulfite, soda, and organosolv processes (Abdelaziz et al. 2016; Bajwa et al. 2019; Gillet et al. 2017; Rajesh Banu et al. 2019). These processes are industrialized primarily due to pulp and paper industry, but agricultural byproducts are also utilized, although less expressively. Kraft pulping is the most common process to recover lignin, being the primary source of technical lignin (Gillet et al. 2017; Rajesh Banu et al. 2019). It mainly results from the pulp and paper industries, representing 85% of global lignin production (Tejado et al. 2007). Lignocellulosic biomass is treated with a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), at high temperatures (150–180 °C) for a few hours until lignin is solubilized in the resulting waste liquor (black liquor) (Abdelaziz et al. 2016). The black liquor is usually used for energy production, making this a self-sufficient process where the burning of lignin gives the energy for the process, but lignin can be recovered and purified through precipitation with the addition of an acid, such as sulfuric acid (H_2SO_4) (Bajwa et al. 2019; Rajesh Banu et al. 2019). The sulfite process is also very common and well established in the pulp and paper industry (Abdelaziz et al. 2016; Rajesh Banu et al. 2019). In this process, biomass is treated with SO_2 and a sulfite base such as calcium, magnesium, sodium, or ammonium (Mandlekar et al. 2018) at high temperatures (120–150 °C) for 3–7 h (Rajesh Banu et al. 2019), and the resulting lignin is referred to as lignosulfonates (Gillet et al. 2017). Lignosulfonates are soluble in water and have a higher molecular weight when compared with kraft lignin. The soda pulping process consists in cooking the lignocellulosic biomass with a solution of NaOH at high temperatures (170 °C) and pressure (10 psi) (Rajesh Banu et al. 2019). This process is usually applied mainly to softwood and grass biomass from agriculture (Gillet et al. 2017; Rajesh Banu et al. 2019), resulting in lignin free of sulfur with low content of impurities (Galkin and Samec 2016).

The organosolv process uses a mixture of water and organic solvent, usually ethanol, methanol, or acetone, at high temperature and pressure (Abdelaziz et al. 2016). The use of organic acids such as sulfuric, chloridric, acetic, formic, and phosphoric acids can catalyze the hydrolysis process (Laskar and Yang 2012; Rajesh Banu et al. 2019). The resulting lignin is sulfur-free, with high purity (Abdelaziz et al. 2016; Gillet et al. 2017) and low molecular weight, and hydrophobic (Vishtal and Kraslawsk 2011). Commercially registered organosolv processes, as Alcell®, Organocell®, Acetosolv®, FormicoFib®, and ASAM®, are already industrialized (Abdelaziz et al. 2016; Gillet et al. 2017). Nonetheless, authors argue the economic viability, as the process has high costs and availability of organosolv lignin is still low (Abdelaziz et al. 2016; Laskar and Yang 2012). The organosolv method is also one of the most studied methods in the literature for the recovery of lignin from agricultural byproducts (Cassoni et al. 2022a, b). Studies using ethanol/water (60:40) to extract lignin from sugarcane bagasse reached high lignin yields (95% and 93%) (Raj et al. 2020; Xu et al. 2020). As for corn, Mouthier et al. (2018) used a low concentration of acetic acid (15%) and was able to recover 72% lignin. Nascimento et al. (2014) recovered 50% lignin from coconut residues using 93% acetic acid,

showing that this byproduct needs harsher conditions, and, yet, the efficiency is lower than lignin extraction on grass species.

The biorefinery industry has also contributed to the development of lignin extraction methods that fit different purposes. In these methods, lignin is usually recovered in the biomass pretreatment process. These pretreatment methods are not yet established at an industrial scale but reveal promising results. Wang et al. (2019) thoroughly reviewed different pretreatment technologies such as acid hydrolysis, alkaline hydrolysis, enzyme hydrolysis, reductive and oxidative fractionation, and combined pretreatment methods. Alkaline hydrolysis is similar to the industrial pulping processes discussed previously but with less treatment severity. The resulting lignin is less condensed, but delignification may not be efficient (Wang et al. 2019). This method is highly used in studies of lignin recovery (Cassoni et al. 2022a, b) and presents good results. For example, a study using only 2% NaOH at 90 °C for 2 h recovered 90.3% of lignin from wheat straw, with high purity (97.4%) (Sun et al. 2018). For corn byproducts, studies also had very good results: 76.37% (Yang et al. 2018), 89.78% (Lei et al. 2013), and 86.6% (Cong et al. 2015). Acid hydrolysis occurs using diluted or concentrated acids, and lignin resulting from this pretreatment process is highly reactive and condensed, being difficult to convert to fuels or chemicals (Wang et al. 2019). Kaur and Kuhad (2019) extracted lignin from a rice byproduct using a combination of H_2SO_4 and NaOH and reached 85% lignin yield with 98% purity. For wheat, using a high phosphoric acid concentration at a low temperature (50 °C) only rendered 23.7% lignin (Wan et al. 2019). The enzymatic hydrolysis method was developed to target polysaccharides through cellulases and hemicellulases (Wang et al. 2019), generating solid residues rich in lignin (Jiang et al. 2017). Usually, this process needs additional pretreatment (physical or chemical) due to the recalcitrance of lignocellulosic biomass (Thomas et al. 2017), and the resultant lignin has low purity (Wang et al. 2019). Reductive and oxidative fractionation involves redox catalysts, and the isolated lignin is very complex and structurally diverse (Wang et al. 2019). Ultimately, since lignin recovery is challenging, some studies combined various pretreatment methods in an effort to overcome drawbacks of lignin recovery (Wang et al. 2019).

Lastly, two new methods are emerging for extracting more environmentally friendly and sustainable lignin: ILs and DES. ILs are organic salts, liquid at room temperature, with high thermal stability, high conductivity, and insignificant volatility (Gillet et al. 2017; Van Osch et al. 2017). There are many possible combinations of salts that form ILs with different properties and that are easily prepared (Van Osch et al. 2017). ILs show high lignin removal capacity, with properties similar to soda and organosolv lignins (Van Osch et al. 2017; Vishtal and Kraslawsk 2011). The main disadvantage of this 'green' method is its high cost and industrial implementation, which still needs further investigation (Gillet et al. 2017; Van Osch et al. 2017). Lignin was extracted from olive pomace using IL [Et3NH][HSO_4] at 150 °C for 2 h, with a yield of 41.5% and high purity (Cequier et al. 2019). For sugarcane bagasse, IL [TEA][HSO_4] allowed a recovery of ~80% lignin (Chambon et al. 2018). DES are a new type of IL-inspired green solvent associated with hydrogen bonds that are characterized by a melting temperature of the eutectic mixture lower

than the melting point of its components (Abbott et al. 2016; Zhang et al. 2012). DES are easily prepared, have a lower cost when compared to ILs, and are considered stable and environmentally friendly since they are biodegradable and nontoxic (Abdullah et al. 2016; Mbous et al. 2017; Zhang et al. 2012). Selected studies show that DES are effective in delignification, yielding high-purity lignin (Satlewal et al. 2018; Tang et al. 2017), but the performance is still inferior compared to ILs (Van Osch et al. 2017). This method was first described in 2003 (Van Osch et al. 2017), and despite the promising results, DES need to be thoroughly studied, and it is still far from industrial application. Cassoni et al. (2022a, b) extracted lignin from grape stalks using DES (lactic acid/choline chloride), reaching 50.2% (±2.3) lignin yield. Li et al. (2018) also tested the same DES in peach byproduct and recovered 87.1% lignin which shows the great potential of DES as a lignin extraction method.

5.2.3.2 Lignin Applications

As an aromatic biopolymer, lignin has interesting bioactive properties such as antioxidant and antimicrobial activities. This bioactivity and other structural characteristics make lignin suitable for several value-added applications.

The antioxidant activity of lignin may vary according to the agricultural source and the extraction method used (Cassoni et al. 2022a, b). Different methods render lignins with different structures, and studies report that lignins with high content of S-units and low molecular weight generally have higher antioxidant activity (Azadfar et al. 2015; Hussin et al. 2015). Studies on apple residues evaluated different extraction methods (autohydrolysis, organosolv, and alkaline) and reported higher antioxidant activity from autohydrolysis and organosolv lignins (García et al. 2011, 2012). On the contrary, lignin extraction of sugarcane byproducts with alkaline and organosolv methods showed that alkaline lignin has the highest antioxidant activity (Bertolo et al. 2019).

The antimicrobial activity of lignin is reported against various bacteria and fungi, especially related to food contamination. Regarding bacteria, it is interesting to note that Gram-positive bacteria seem more susceptible to lignin (Dong et al. 2011; El-Nemr et al. 2019; Rai et al. 2017).

Nonetheless, a study using corn stover lignin reported the inhibition of *Escherichia coli*, *Salmonella enterica*, *Bacillus subtilis*, and *Staphylococcus aureus* (Wang et al. 2018). Tests on fungi also revealed satisfactory results. Jonglertjunya et al. (2014) reported a higher antifungal activity against *Alternaria alternata* using sugarcane bagasse lignin extracted from sugarcane bagasse when compared with commercial lignin. Lignin from apple wastes was also effective against *Aspergillus niger*, causing delayed growth and morphological modifications (García et al. 2017).

These bioactivities are especially interesting for food packaging applications, but lignin is also incorporated in polymers for the enhancement of mechanical properties. Lignin from corn stover was extracted and used to improve thermal stability and tensile strength of polylactic acid (PLA) (Gao et al. 2019). Other reported features are, for example, UV resistance, flame retardancy, and elasticity (Phaodee et al.

2015; Song et al. 2018; Xie et al. 2015). Various agricultural byproducts were used to extract lignin to be further incorporated in different polymers. Lignin from wheat and rice byproducts incorporated in polystyrene increased UV resistance (Ma et al. 2017); lignin from coconut had a role in the thermal stability, antioxidant activity, and UV resistance (Avelino et al. 2019); and lignin from rice byproducts applied in polypropylene improved water absorption and thickness swelling (Karina et al. 2017).

Another interesting application is lignin as a delivery system of active compounds. The controlled release of these compounds improves their efficiency due to the protection of extrinsic factors (Costa et al. 2017; de Oliveira et al. 2014). Lignin from agricultural byproducts is often used to encapsulate pesticides and fertilizers. Controlled release of urea using lignin from sugarcane, corn, and wheat byproducts was proposed (Elhassani et al. 2019; Gu et al. 2019; Jiao et al. 2018). Olive wastes' lignin was also studied as coating for triple superphosphate fertilizer (Fertahi et al. 2020). Concerning pesticides, spent mushroom substrate was used to develop a lignin-based nanocarrier of plant protection drugs (Beckers et al. 2019). Wheat straw was also used to extract lignin that was further functionalized as a hydrogel composite for controlled release of a pesticide (Sun et al. 2016). The controlled release of pesticides is essential because it allows a more targeted application and reduced quantities, decreasing their environmental impact (Yearla and Padmasree 2016).

There are many other possible applications of lignin reported in the literature, such as dispersant, fertilizer, pesticide, and bioremediation agent, among others. Cleary, lignin is a versatile biopolymer that has many interesting properties that allow a wide variety of applications with a promising future.

5.3 Future Perspectives

Today's society, environment, and industries need to change from a linear economy production toward sustainable and biocircular model of production and consumption (Camilleri 2021). These demands have been recognized and gained awareness not only for researchers of biotechnology, environment, and food science and technology areas but also for business developers and governmental sectors to work for the same objectives to decrease the environmental and social issues by promoting a suitable and correct management of natural resources and at the same time create new revenue streams (Torres-León et al. 2018). The biorefinery approach is gaining research and industrial interest as well for a suitable management and valorization of several lignocellulosic biomasses toward obtention of multiple products by utilizing waste streams, upcycling co-products and byproducts, having the capacity of increasing the efficiency of the industrial value chain, and reducing their associated costs and negative environmental impacts (Liu et al. 2021). Presently, there is now a time demanding sustainable and more natural foods, materials, chemicals, and fuels (among others) with highly valued properties focused on nutritional quality, well-

being, and biodegradability and renewability. In this regard, agricultural lignocellulosic byproducts have been highlighted as promising raw materials with high potential value due to their nature, structural and bioactive composition, and renewability, as well as high accessibility and low cost due to their massive production as waste streams industrially.

As described in Sect. 5.2, complex carbohydrates (cellulose, hemicellulose, and lignin polymer) are the most significative constituents present in this kind of waste but also contain organic acids, lipids, proteins, and ash in less extension, of which all of them can be isolated and extracted under biorefinery approach by the combination of traditional and novel techniques to be applied as raw materials or ingredients for industrial objectives, compensating the initial investment, increasing profitability and rentability, and subsequently reducing waste generation and contamination. Biorefinery systems are known as cascading processes to produce multiple products. For example, these systems can make multiple high-value goods such as biofuels (biomethane), biochemicals (antioxidants), and biomaterials (fibers and composites) and also proteins and fibers, among other nutritional molecules for human consumption (foods and feed) (Tsegaye et al. 2021) (Fig. 5.3). Additionally, the biorefinery approach could be totally integrated/coupled with well-consolidated biotechnological processes such as anaerobic digestion, which in turn can generate biogas and fertilizer simultaneously.

The development of a single integrative process under biorefinery context by unifying several specific technologies and methods could boost the total exploitation of these biomasses without compromising the environment and economy of industries as well as will allow the delivery of sustainable management process and subsequently different bioproducts, fulfilling the EU directives.

5.4 Conclusions and Final Remarks

The agricultural lignocellulosic byproducts can be part of the solution to the world's issues threatening economy and sustainability since these materials are rich in several natural biomolecules (cellulose, hemicellulose, and lignin, among others) and can be expected as low-cost raw materials with easy accessibility to obtain several value-added bioproducts. Seeking for the substitution of the traditional techniques by more sustainable, cleaner, and eco-friendly practices is a vital step to achieve a correct valorization of byproducts and generate the desirable bioproducts, including biofuel, biopolymers, biomaterials, pharmaceutical coatings, proteins/enzymes, and foods. The integration of biorefinery approach could boost the bioeconomy transition by bringing these products with high industrial demand, but despite its high promising advantages and features, biorefineries still need process optimization, efficient integration, high recovery yields, and products and process profitability as well as scalability for its application in an industrial environment. As it was described in this chapter, many technical and scientific strategies for the conversion of lignocellulosic waste involving different multidisciplinary areas

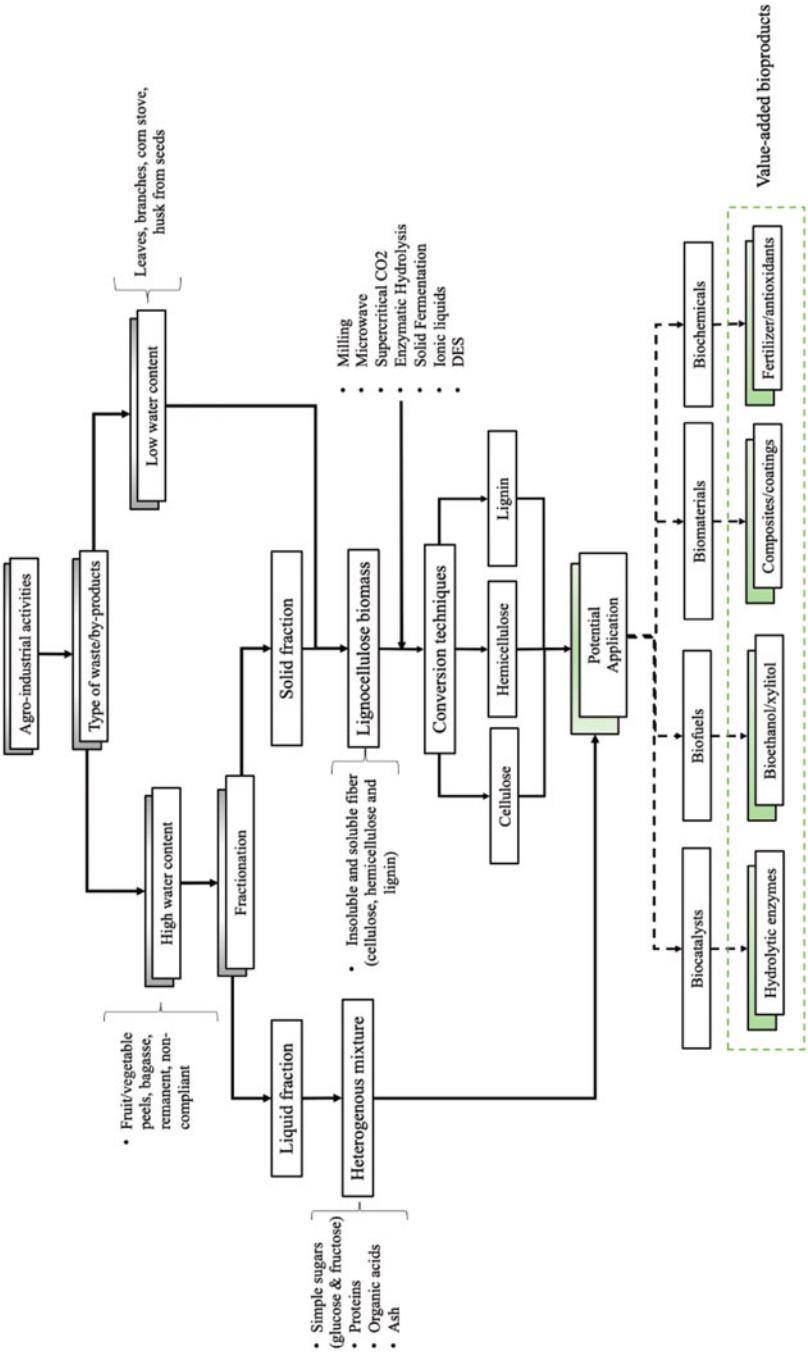

Fig. 5.3 Fractionation process under biorefinery approach for lignocellulosic waste valorization to the development of different valuable bioproducts

have been idealized and carried out at laboratory scale with promising results, which in the near future can help to develop sustainable biorefinery systems and address a circular bioeconomy, covering the gap between waste valorization to product development and environmental protection.

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Chapter 6
Bioactive Peptides from Protein-Rich Waste

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Abstract Waste is produced by agro-industries from plant products and animal products in large quantities. This waste, although an economically viable source of nutrients, is usually devalued and used in agriculture or animal feed. Most of this raw material contains many compounds of economic interest, such as proteins. Proteins can be transformed into peptides through chemical, enzymatic, or microbiological processes. The hydrolysate-protein or peptides that are generated in these processes have high antioxidant, antihypertensive, and antimicrobial activities, among others. In addition, this hydrolysate-protein can also contribute to the technological characteristics of food products as they can improve solubility, emulsification capacity, and gel formation, among others. Thus, the objective of this chapter was to elucidate the methods of peptide production, as well as their technological and biological properties.

Keywords Residue · By-products · Antioxidant · Antihypertensive

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6.1 Introduction

The food industry is increasingly aware of consumer demand for proteins from sustainable sources. Consumers, in turn, have demanded food products that, in addition to providing nutrients, cause the least environmental impact during their production or are produced by eco-friendly industries (Oliveira Filho et al. 2020). In this sense, residues and by-products from the food industry end up being an environmental problem due to their low use in animal feed or agriculture. The use of these raw materials as an ingredient in other foods can promote financial valorization, increasing the industry's profit, in addition to meeting consumer expectations for eco-friendly products (Lemes et al. 2021a, b).

The waste of raw material that is not consumed or used in any other process amounts to about 1.3 billion tons (Ishangulyyev et al. 2019), and the economic losses from this waste can cost about 680 billion dollars annually (Dora et al. 2020). This is a bad scenario in a world where hunger is still a worrying factor as it affects more than 1.2 billion people who do not have access to food and also do not know if what they eat is safe or if their diet is nutritionally correct or reliable (FAO 2013).

These residues are known to contain compounds of interest to the food and pharmaceutical industry, such as bioactive compounds, phenolic compounds, and proteins, among others (Egea et al. 2021; Lemes et al. 2021a, b; Oliveira Filho et al. 2022; Sousa et al. 2021). Protein-rich residues have been extensively studied by food science due to the great need of the industries for this compound that can be used in the most diverse applications. Protein has been sought after by industries because it is widely used in its raw or hydrolyzed form to improve food properties such as solubility, emulsification, and gel formation, as well as is able to represent a source of protein for the diet (Lemes et al. 2016a, b). In addition, protein hydrolysates may present important biological activities for human health, such as antioxidant, antimicrobial, and antihypertensive, among others (Lemes et al. 2020a, b).

In this way, the use of waste and by-products from the industry seems to be a viable strategy to meet the most diverse demands. Thus, the objective of this chapter was to elucidate the methods of peptide production, as well as their technological and biological properties.

6.2 Waste Generation

The agribusiness and food sector plays an important economic role in the world, with an estimated turnover of more than 5 trillion dollars annually (TWB 2017), which includes the production of fruits, vegetables, grains, milk, meat, and fish, among other raw materials. Most of these products obtained by these sectors are used for human and animal consumption and also for energy production (FAO 2017; Sadh et al. 2018), in addition to other noble applications.

The agribusiness and food sector has a great impact, especially in underdeveloped or developing countries, as it guarantees domestic supply and exports, in addition to contributing to economic growth and job creation, strengthening rural economies and food and nutrition security, improving the population's quality of life, and promoting raw materials that, when processed properly, have high added value. In addition, the processing of agro-industrial raw materials promotes their transformation, providing diversity of food products and prolonging availability by increasing the shelf life and also the possibility of distribution in distant regions of the globe (Lemes et al. 2020a, b, 2021a, b).

However, during the different stages of the production chain, including harvesting, post-harvesting, slaughtering, transport, processing, storage, and consumption, among others, losses are verified that can reach up to 50% in some specific products, but on average they represent about one-third of everything produced worldwide. Additionally, the adoption of inappropriate or non-optimized production processes can further increase the generation of agro-industrial waste (Arah et al. 2016; Lemes et al. 2020a, b).

A large part of these wastes end up becoming an environmental issue, since, in some cases, wastes are highly resistant to degradability, resulting in accumulation and, thus, becoming a potential pollutant for the environment and for humans (Sadh et al. 2018). Still, in general, these wastes have a high biochemical oxygen demand, which can impact the degradation process, since they result in a decrease in oxygen, which can result in the death of some microorganisms responsible for their degradation (Bendicho and Lavilla 2019).

It is important to highlight that the waste generated in agribusiness has nutritional components from native food matrices and can be used as low-cost raw material and easily available to obtain products with greater added value, in addition to contributing to the adoption of environmentally appropriate processes (Lemes et al. 2016a, b, 2020a, b, 2021a, b), mitigating, at least in part, the impacts caused by the sector.

Considering the issues mentioned above, it is important that the waste generated be seen as an integral part of the economic system of the regions where they are produced and processed, since they impact on expenses for their correct disposal but also generate revenue for those who process, aiming at obtaining improved products. In this way, it is remarkable that the waste processing and transformation sector must be included in all public policies, as a mechanism for mitigating negative impacts on society, health, and the environment (DEFRA 2011).

In general, agro-industrial wastes contain a variety of components with variability in their composition, which include fibers, carbohydrates, minerals, and, mainly, a high content of proteins, which can be used to obtain biologically active molecules such as peptides, and these in turn can be included in various products, due to their technological role, in pharmaceutical, food, and beverage industries (Lemes et al. 2021a, b).

6.2.1 Waste: Vegetal and Animal Origin

Agro-industrial waste can be divided into products of plant and animal origin (Fig. 6.1) and includes a diversity of materials and, consequently, a wide variety of waste with totally different characteristics (Table 6.1), which ends up making its use a complex task by the difficulty of optimizing a method or process that can be used for all raw materials (Lemes et al. 2021a, b). Table 6.1 presents the estimated losses in some production chains, the type of waste generated, and characteristics and causes of the loss of the main agro-industrial raw materials produced and used in the world.

Table 6.1 shows the estimated losses in some production chains, the type of waste generated, and characteristics and causes of the loss of the main agro-industrial raw materials produced and used in the world.

Presently, great attention has been paid to residues rich in proteins, which can be used in the production of bioactive peptides from suitable processes, including the use of solvents, enzymes, and fermentations (Fig. 6.1), for example—see more details in item 3 (Prado et al. 2020; Ying et al. 2021).

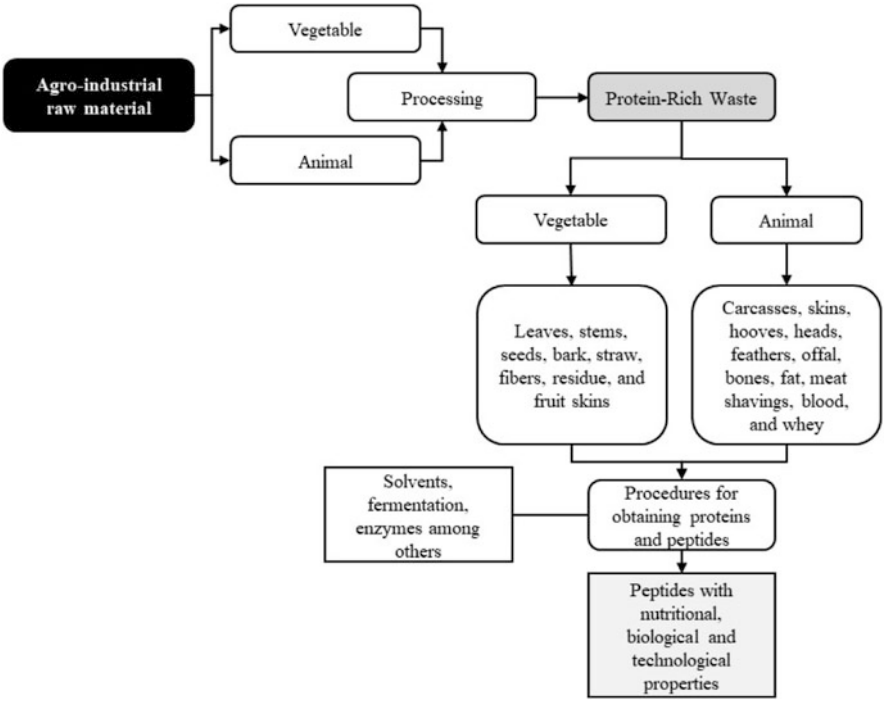

Fig. 6.1 Main waste generated from the processing of raw materials of vegetable and animal origin to obtain bioactive peptides

Table 6.1 Estimated losses in some production chains, types of waste generated, and characteristics and causes of loss of the main agro-industrial raw materials used in the world

Raw material	Estimated loss (%)	Waste type	Characteristic (1)/cause of loss (2)	References
Cereals	~35%	– Liquid residues: rice milling wastewater, parboiled rice effluent, corn steep liquor, and bakery wastewater	(1) ↑ Polluting ↑ [ ] organic load, solid waste, and nutrients	Hassan et al. (2021), Lemes et al. (2020a, b)
		– Solid: corn pericarp, corn grits, and brewer's spent grain	(2) Harvest, transport, and storage (insects, mites, birds, rodents, fungi, and bacteria)	
Fruits, vegetables, roots, and tubers	~40–50%	Leaves, stems, seeds, bark, straw, fibers, bagasse, and fruit skins	(1) ↑ [ ] Carbohydrates (starch, cellulose, and hemicellulose), lignin, organic acids, minerals, and vitamins	Lemes et al. (2020a, b)
			(2) Cleaning, processing, cooking, and packaging	
Meat	~23%	Carcasses, skins, hooves, heads, feathers, viscera, bones, fat, meat trimmings, and blood	(1) ↑ [ ] Proteins, lipids, and minerals	Karwowska et al. (2021)
			(2) Consumption losses, industrial processing, distribution, inadequate storage conditions, and failures in the freezing process	
Dairy industry	~4 to 11 million tons/year	Whey, dairy sludges, and wastewater (processing, cleaning, and sanitary)	(1) ↑ Pollutant potential, ↑ [ ] proteins, lactose, vitamins, and minerals	Lemes et al. (2020a, b), Ahmad et al. (2019)
			(2) Milk obtaining, transport, storage, and production process	
Fish waste	~60% of the processed fish are discarded	Muscle (15–20%), viscera (12–18%), bones (9–15%), heads (9–12%), scales (5%), and skin and fins (1–3%)	(1) ↑ Protein (skin), calcium (trimmings and bones), and lipids (head, intestines, and bones)	Tacias-Pascacio et al. (2021), Tesfay and Teferi (2017)
			(2) Capture; transportation, handling, and processing and others	

Bioactive peptides are protein fragments that can contain about 2–20 amino acids and exhibit some effects on body functions and conditions, influencing health (Lemes et al. 2016a, b; Meena et al. 2020). These peptides may exhibit diverse biological activities, such as antihypertensive, antioxidant, anti-inflammatory, antimicrobial, immunomodulatory, and other that include behavioral, neurological, hormonal, gastrointestinal, and nutritional (Capriotti et al. 2016; Lemes et al.

2020a, b). They can be used industrially in the production of drugs and, mainly, in the development of foods, with great influence on the technological properties, such as the water and oil retention capacity, viscosity, and foaming, besides acting as a color preservative, acidity regulator, sweetening agent, emulsifier, and flavor enhancer, among other properties (Agyei et al. 2016; Lemes et al. 2021a, b).

The processing of vegetable raw materials commonly includes the steps of cleaning, processing, cooking, and packaging (US EPA 2012) and can result in thousands of tons of leaves, stems, seeds, bark, straw, fibers, bagasse, and fruit skins, among others (Ezejiofor et al. 2014). Residues of vegetable origin present in their composition high levels of carbohydrates (starch, cellulose, and hemicellulose), lignin, organic acids, minerals, and vitamins (Kumar et al. 2020) and also high concentrations of proteins (Oliveira Filho et al. 2021). Among the plant agro-industrial residues that are commonly used to obtain bioactive peptides due to their high protein content, we can mention (residue/protein content): cottonseed by-product/~30.0% (Oliveira Filho et al. 2021), sunflower by-product/27.8% (Prado et al. 2020), corn oil processing by-product/~10.6% (Sousa et al. 2021), okara from soybean/~25% (Guimarães et al. 2018), and bean by-product/~22.0% (Segura-Campos et al. 2014) and several other sources available for use.

The processing of raw materials of animal origin can generate large amounts of carcasses, skins, hooves, heads, feathers, viscera, bones, fat, meat trimmings, blood, and other animal fluids (Ockerman and Hansen 1999; Waldron 2007). Waste of animal origin mainly presents high concentrations of proteins and also lipids and minerals (Jain and Anal 2017; Jayathilakan et al. 2012; Maysonnave et al. 2020). Among the residues of animal origin commonly used to obtain bioactive peptides due to their high protein content, we can mention (residue/protein content): fish by-product/49.22–57.92% (Tacias-Pascacio et al. 2021), fish viscera/up to 65% depending on the species (Villamil et al. 2017), bovine blood/17.3% (Duarte et al. 1999), feather meal/~91.5% (Lemes et al. 2016a, b), and whey protein/35–80% depending on the extent of protein concentration (%) (Kottahachchi Kankanamge 2018), among other protein-rich residues.

Some practical examples of the application of bioactive peptides have already demonstrated their potential when applied in food formulations, including increased water retention capacity in meat products, emulsifying capacity, emulsion stabilizer, rheological quality improver, gel formation capacity, and foam stabilizer, role in reducing loss and shrinkage during cooking and frying of products, and also as a reducing agent of lipid peroxidation in foods, acting as a substitute for synthetic antioxidants (Zaky et al. 2021)—see item 4 for more detail.

Due to the biological, technological, and nutritional potential, and also due to the large production of agro-industrial residues of animal and plant origin. It is important to establish adequate processes for obtaining bioactive peptides, so that it is possible to obtain molecules with application in food, beverage, and drug formulations, in addition to enabling the development of processes that result in the use of waste and lead to the mitigation of environmental damage.

6.3 Protein and Peptide Production from Waste

Generally, bioactive peptides from protein-rich wastes are released through chemical and biological hydrolyses (i.e., enzymatic and fermentation processes), which are the focus of this chapter. However, emerging processes utilizing high hydrostatic pressure (Chen et al. 2021), ultrasound (Mala et al. 2021; Ruan et al. 2020), microwave (Li et al. 2019), pulsed electric fields (Franco et al. 2020), and subcritical water hydrolysis (Ahmed and Chun 2018) can be applied single or together with traditional methods to produce peptides from protein sources. Table 6.2 summarizes some examples of traditional methods to produce bioactive peptides.

Before reaction of hydrolysis, protein-rich wastes are prepared according to their specificities, being steps simpler (e.g., milling the substrate until a powder) or more complexes (e.g., protein separation from the other compounds). Grinding and sieving steps are commonly applied to some solid wastes (e.g., vegetable, cereal, and meat) to reduce and standardize particle size (Mala et al. 2021; Meshginfar et al. 2018). Wastes with high lipid contents are defatted prior to hydrolysis (Fathi et al. 2021; Moayedi et al. 2018; Singh et al. 2019). Plant tissue residues can be submitted to a solid-liquid extraction step (i.e., using an aqueous buffer and organic or inorganic solvents, among others) to recover proteins from the other compounds in the matrix (Oliveira Filho et al. 2021; Ramirez et al. 2021; Silva and de Castro 2020; Tao et al. 2018). Protein from residues can be isolated through pH-shifting precipitation (Lima et al. 2019; Meshginfar et al. 2018; Nourmohammadi et al. 2017)—a procedure that solubilizes protein fraction using acid and alkaline solutions and precipitates it at its isoelectric pH (Surasani 2018)—for further hydrolysis. In other cases, pretreatment methods (e.g., high hydrostatic pressure, microwave, ultrasound, thermal, chemical reagents, etc.) can be applied to the protein source to facilitate the extraction or improve the subsequential hydrolysis process (Cheong et al. 2018; Fathi et al. 2021; Perreault et al. 2017; Thoresen et al. 2020).

6.3.1 Traditional Hydrolysis Process Applied to Obtain Bioactive Peptides

6.3.1.1 Chemical Hydrolysis

Chemical hydrolysis utilizes acid or alkaline reagents to cleave bonds in the protein chain, releasing peptides and free amino acids. Although chemical hydrolysis is a simple method, it is limited in specificity and control of process parameters (Ulug et al. 2021). Due to the unspecific cleavage of peptide bonds caused by chemicals, the reproducibility of biological activities of peptides is compromised, which limits the application of protein hydrolysates (Nasri 2017). Hydrolysis with chemicals is combined with heating, where extreme temperature and pH conditions could damage amino acids (Wisuthiphaet et al. 2016) and affect hydrolysates' nutritional quality

Table 6.2 Some examples of traditional hydrolysis methods to obtain peptides from protein-rich wastes

Protein source	Method	Specifications	Main results	Additional comments	References
Low-value marine fishes	Acid and enzymatic hydrolysis	Evaluation of HCl concentration (4–8 M) and temperature (80–100 °C) for 90 min; evaluation of Alcalase® concentration (6–10%), temperature (50–70 °C), pH (6–8), and time (10–30 min)	DH of 50.7% at 4 M HCl and 100 °C or 88.9% at 6% Alcalase® for 90 min, 61.23 °C for 27.36 min	Glu was the most abundant amino acid in the hydrolysates followed by Asp/Ala (acid hydrolysis) and Asp/Lys/Leu/Val (enzymatic hydrolysis)	Wisuthiphaet et al. (2016)
Salmon waste	Acid and enzymatic hydrolysis and microbial fermentation	Acid (2% formic acid/37 °C/150 rpm/8 days) and enzymatic (Flavourzyme® at 1:100 enzyme: substrate ratio/pH 7.0/37 °C, 150 rpm/12 h) hydrolysis and microbial fermentation (1% acid lactic bacteria inoculum/37 °C/150 rpm/8 days)	DH of ~60% and ~56% for enzymatic and acid hydrolysis, respectively, and ~44% for microbial fermentation	~87%, ~57%, and 35% of protein content in the acid and enzymatic hydrolysis and microbial fermentation, respectively	Rajendran et al. (2018)
Chicken feathers	Alkaline hydrolysis	Use of 1 M NaOH during the evaluation of solution/substrate ratio (3:1/6:1/9:1), speed (150–200 rpm), and time (16–32 h)	Maximum protein yield (~41%) was obtained at solution/substrate ratio of 9:1, 200 rpm, and 32 h. Speed and time did influence significantly the yield values	Hydrolysate presented two peptide fractions with molecular weight of 130 and 250 kDa, besides a mixture of peptides close to 10 kDa	Dąbrowska et al. (2022)
Chicken blood	Enzymatic hydrolysis	Evaluation of enzyme/substrate ratio (3.5–6.5%), temperature (54–62 °C), pH, (7.5–8.5), and time (90–120 min) using Alcalase®	Maximum DH (25.9%) was obtained at enzyme/substrate ratio of 6.5%, 50 °C, pH 8.5, and 120 min	Hydrolysate presented small peptides with molecular weight near to 14.4 kDa	Alves et al. (2021)
Porcine blood	Enzymatic hydrolysis	Evaluation of six proteases (Alcalase®, Flavourzyme®,	Maximum DH (13.4% and 12.9%) were obtained using	High DH (9.17% and 7.1%) were also achieved using	Jin et al. (2020)

		Protamex®, Neutrase, papain, and trypsin) at 50 °C, pH 7.0, and 1% blood proteins (globulin and albumin) until 5 h of reaction	trypsin and papain for porcine globulins and albumins, respectively	Alcalase® for both blood proteins	
Chia seed meal	Enzymatic hydrolysis	Evaluation of four proteases (Alcalase®, pepsin, trypsin, and α-chymotrypsin) under their optimal conditions and different enzyme/substrate ratio and 5% chia seed protein isolate	Maximum DH (38%) was obtained using Alcalase® followed by pepsin (15%), α-chymotrypsin (~12%), and trypsin (11%)	Hydrolysate obtained by pepsin showed the highest biological activity in terms of inhibitory potential of angiotensin-converting enzyme	San Pablo-Osorio et al. (2019)
Sorghum spent grain	Enzymatic hydrolysis	Use of Purazyme® (50 °C) and Flavourzyme® (55 °C) at pH 7.0, enzyme/substrate ratio of 5: 100, and 1% sorghum spent grain	DH and protein recovery corresponded to 10.9% and 21.9%, respectively	Hydrolysate presented small peptides (0.5–2 kDa) with biological properties in terms of antioxidant, antibacterial, and antidiabetic activities	Garzón et al. (2022)
Cottonseed waste	Enzymatic hydrolysis	Evaluation of hydrolysis performance using 1:17 enzyme/substrate and Flavourzyme® (60 °C, pH 7.0), Neutrase® (40 °C, pH 7.0), and Alcalase® (55 °C, pH 8.0) for 100 min	DH were 40.3–47.2% for Alcalase®, 29.7–36.4% for Neutrase®, and 27.2–27.5% for Flavourzyme®	Hydrolysates showed biological properties in antioxidant, antimicrobial, and antihypertensive activities	Oliveira Filho et al. (2021)
Spent coffee grounds	Microbial fermentation and enzymatic hydrolysis	Fermentation was carried out with *Bacillus clausii* at 37 °C for 39 h. Fermented spent coffee grounds were enzymatically hydrolyzed by pepsin (pH 2.0, 37 °C, 3 h) and pancreatin (pH 8.0, 37 °C, 3 h)	Microbial fermentation increased the amounts of total protein hydrolysates by 1.2-fold compared to non-fermented spent coffee grounds	Microbial fermentation of spent coffee grounds increased the abundance of peptides that displayed biological properties such as antioxidant, angiotensin-converting enzyme inhibitory,	Ramirez et al. (2021)

(continued)

Table 6.2 (continued)

Protein source	Method	Specifications	Main results	Additional comments	References
				and dipeptidyl peptidase-IV inhibitor activities	
Tomato seed meal	Microbial fermentation	Fermentation was carried out in a medium containing 5% tomato seed meal and 2% *Bacillus subtilis* inoculum at 37 °C for 24 h	Proteases from *Bacillus subtilis* cleaved proteins of tomato seeds into short peptides	Production of small peptides (<1 kDa) with different aromatic and hydrophobic amino acid residues and with antioxidant angiotensin-converting enzyme inhibitory activities	Moayedi et al. (2018)
Eggshell membranes	Microbial fermentation	Fermentation was carried out in a medium containing 5% of eggshell membranes with *Lactobacillus plantarum* at 30 °C. Parameters such as initial pH (4–8) and time (6–72 h) were varied to process optimization	Fermentation at an initial pH of 8.0 for 36 h resulted in maximum protein concentration (177.3 mg/g) and degree of hydrolysis (25.1%)	Hydrolysates presented functional (foaming and emulsification capacities) and biological (antioxidant and angiotensin-converting enzyme inhibitory activities) properties	Jain and Anal (2017)

DH degree of hydrolysis

and technological/biological functionalities. In addition, chemical hydrolysis is difficult to control (Ishak and Sarbon 2018) and could generate undesirable compounds and large quantities of chemical effluents. At the end of chemical hydrolysis, a neutralization step is required to further the application of hydrolysates (Nikhita and Sachindra 2021).

Hydrochloric acid (HCl) is used most in acid hydrolysis to obtain peptides from protein-rich wastes. Some examples include the hydrolysis of low-valued marine fishes using HCl (4–6 M) and high temperature (80–120 °C) (Wisuthiphaet et al. 2016) and the hydrolysis of chicken blood protein combining HCl (0.01–0.03 M) and heating (30–70 °C) (Nikhita and Sachindra 2021). Formic acid aqueous solution (2%, v/v) has also been applied in the hydrolysis of a salmon by-product (Rajendran et al. 2018).

Alkaline hydrolysis commonly uses sodium or potassium hydroxides (NaOH or KOH) (Borrajo et al. 2019) to cleave protein chain bonds and release peptides. Low molecular weight peptides and sodium and potassium salts of free amino acids could be formed depending on the alkaline reagent (Kalambura et al. 2016). Slaughterhouse wastes have been submitted to alkaline hydrolysis for solubilizing and extracting hydrolyzed protein fragments with the added benefit of destroying pathogens and prions (Adhikari et al. 2018). Recently, alkaline reagent has been applied to hydrolyze chicken feathers and release keratin peptides (Dąbrowska et al. 2022).

6.3.1.2 Enzymatic Hydrolysis

Enzymatic hydrolysis utilizes animal, plant, or microbial proteases to cleave protein chains and release peptides from waste matrices. It is carried out under controlled and mild reaction conditions (pH, temperature, substrate/enzyme ratio, and substrate concentration) (Ishak and Sarbon 2018) that are adjusted according to the protein source and enzyme extracts. Several advantages are attributed to enzymatic hydrolysis and made it the most applied technique to produce bioactive peptides: high enzymatic specificity, non-formation of toxic compounds, non-use of chemicals or organic solvents, process reproducibility, and ease of adjustment and adaptation of operational parameters. Moreover, the amino acid composition of hydrolysates obtained enzymatically is closed to that protein substrates, with little differences according to the applied enzymes (Nasri 2017). In contrast, the high costs of commercial enzymatic extracts, the release of peptides in a high-diluted medium, and the low peptide yields are some barriers that still limit the application of enzymes on large scales.

Enzymatic hydrolysis can apply a single protease (peptidase) extract (Lima et al. 2019) or combine different proteases in simultaneous (Lu et al. 2019; Mangano et al. 2021) or sequential reactions (Marson et al. 2019; Yaghoubzadeh et al. 2020). Endopeptidases act on protein chain internal bonds, liberating peptides of various sizes, whereas exopeptidases act at peptide ends on C- or N-terminal and liberate single amino acid residues or small peptides. These differences in mode of action need to be considered during the choice of protease for protein hydrolysis (Tavano

2013). Commonly, endopeptidases are used at the first stages of hydrolysis, and then exopeptidases are added. Commercial enzymes usually applied for bioconversion of protein-rich wastes include Alcalase® (Alves et al. 2021; Oliveira Filho et al. 2021), Flavourzyme® (Korkmaz and Tokur 2022), Protamex® (Pezeshk et al. 2019), Purazyme® (Garzón et al. 2022), Neutrase (Yuan et al. 2018), trypsin (Kaewsahnguan et al. 2021), α-chymotrypsin (Ambigaipalan and Shahidi 2017), pepsin (San Pablo-Osorio et al. 2019), bromelain (Coscueta et al. 2021), and papain (Jin et al. 2020), among others. Novel plant or microbial proteases (Corrêa et al. 2019; Delgado-García et al. 2019; Li et al. 2022; Rieger et al. 2017; Saidi et al. 2018; Zanutto-Elgui et al. 2019) are also explored in the hydrolysis of protein wastes, indicating the potential of new protease preparations to produce bioactive peptides.

Enzyme specificity and hydrolysis reaction conditions impact the amino acid sequence and size of the peptides produced, both crucial in the bioactivity of hydrolysates (Gao et al. 2021). In this sense, studies are carried out to evaluate the behavior of different proteases against a protein substrate's conversion into peptides (Jin et al. 2020; Oliveira Filho et al. 2021; Yuan et al. 2018) and optimize the hydrolysis conditions (Coscueta et al. 2021; Korkmaz and Tokur 2022; Singh et al. 2019; Unnikrishnan et al. 2021). Enzymatic hydrolysis is usually monitored by measuring the degree of hydrolysis (DH) (Alves et al. 2021; Jin et al. 2020; Kaewsahnguan et al. 2021; Korkmaz and Tokur 2022; Marson et al. 2019) and can be performed up to a desirable DH value. In many cases, the optimization of enzymatic hydrolysis considers the highest DH achieved under certain reaction conditions (Korkmaz and Tokur 2022).

Enzymatic hydrolysis can be applied as a single method or after a protein extraction, concentration, or isolation procedures, such as solid-liquid extraction (Oliveira Filho et al. 2021; Tao et al. 2018) and pH-shifting step (Rocha et al. 2018). Before enzymatic hydrolysis, protein suspension is often heated (>85 °C) to inactivate endogenous enzymes (Lima et al. 2019; Yaghoubzadeh et al. 2020; Yu et al. 2017). Enzymatic hydrolysis ends with medium heat to inactivate proteases (Korkmaz and Tokur 2022; Mangano et al. 2021). Afterward, the hydrolysates are submitted to solid-liquid separation (e.g., centrifugation) and refining steps (e.g., peptides' concentration and fractionation) (Lima et al. 2019; Pezeshk et al. 2019; Unnikrishnan et al. 2021).

6.3.1.3 Microbial Hydrolysis

Although enzymatic hydrolysis has been used extensively to produce peptides from protein-food wastes, microbial fermentation by proteolytic species has also been demonstrated to be an interesting strategy. This approach employs proteolytic microorganisms to hydrolyze proteins and release peptides. The activities of various proteases derived from microbial specie in a protein-containing medium may result in the generation of peptides and free amino acids (Moayedi et al. 2016). The single-step process is one of the most significant advantages of microbial fermentation, allowing the production of other target metabolites together with the peptides and

obtaining hydrolysates rich in bioactive compounds. As stated by Nasri et al. (2022), microbial fermentation also avoids the costs of enzyme extraction and purification related to enzymatic hydrolysis. However, microbial fermentation is disadvantageous from the view of yield (Nasri 2017) and the number of downstream steps to obtain pure peptides.

Because of their proteolytic properties, *Bacillus* species are frequently applied among microbial species. Some examples include the use of *Bacillus* species to produce hydrolysates containing peptides from spent coffee grounds (Ramirez et al. 2021), tomato wastes (Moayedi et al. 2018), corn gluten meal (Jiang et al. 2020), soybean meal (Ruan et al. 2020), and chicken feathers (Alahyaribeik et al. 2021). Acid lactic bacteria from *Lactobacillus* genera have also been used to produce peptides from protein-rich wastes, such as rice-starch waste (Babini et al. 2020), eggshell membranes (Jain and Anal 2017), tomato seed meal (Mechmeche et al. 2017), sea bass wastes (Chen et al. 2021), and salmon viscera (Rajendran et al. 2018). Safe strains in food industry such as *Saccharomyces cerevisiae*, *Aspergillus oryzae*, and *Streptococcus thermophilus* were evaluated to convert turbot skin protein into hydrolysates containing peptides (Fang et al. 2017). Other microorganisms such as *Chryseobacterium* sp. and *Monascus purpureus* were utilized in the production of peptides from chicken feather (Fontoura et al. 2019) and porcine liver (Yu et al. 2017), respectively.

In microbial fermentation, the nature of protein-rich waste, the presence of other nutritional compounds, the specificity of microbial proteases, and the processing conditions influence the type of peptides produced (i.e., molecular weight and amino acid composition) and their biological activities (Nasri et al. 2022). In this sense, studies have been conducted to determine the optimal fermentation conditions to produce peptides (Jain and Anal 2017; Jiang et al. 2020). Similar to enzymatic hydrolysis, microbial fermentation is followed by solid-liquid separation step to separate the hydrolysate and submit it to refining approaches (Fang et al. 2017; Fontoura et al. 2019; Ramirez et al. 2021).

6.3.2 *Refining Techniques Applied to Bioactive Peptides from Protein-Rich Wastes*

Hydrolysates from protein-rich wastes should be submitted to refining steps that allow the concentration/purification of peptides for later characterization (i.e., molecular weight distribution and amino acid sequence) and evaluation of technological and biological properties. The number of refining steps involved will depend on the extraction method, the composition of the final hydrolysate, and the degree of purification required.

Ultrafiltration (UF) is typically applied to concentrate and fractionate peptides in different molecular weights from a crude protein hydrolysate (Pezeshk et al. 2019; Saidi et al. 2018; Unnikrishnan et al. 2021; Yaghoubzadeh et al. 2020; Yuan et al.

2018). The principle of UF is the permeability differences of liquid constituents through a membrane (Lemes et al. 2016a, b). Membranes with high nominal molecular weight cutoffs (MWCO, 20–100 kDa) are used to separate peptides and non-hydrolyzed proteins or other compounds in the hydrolysate, whereas membranes with intermediate or low MWCO (1–10 kDa) fractionate and concentrate desirable peptides (Nasri 2017).

Partial purification of hydrolysates containing peptides can be achieved by salt precipitation followed by dialysis (Jain and Anal 2017). Highly purified peptide-rich fractions are accomplished using chromatographic methods and occur due to the interaction of peptides with the stationary and mobile phases. In general, peptides are purified by a sequence of chromatography steps (Lemes et al. 2016a, b). Peptides of specific molecular weights can be concentrated using size-exclusion chromatography (Ambigaipalan and Shahidi 2017; Zheng et al. 2018). Reverse-phase (Kaewsahnguan et al. 2021; Tao et al. 2018), ion-exchange (Li et al. 2022; Tao et al. 2018), and affinity (Rayaprolu et al. 2017) chromatography can be applied to separate peptides according to their hydrophobicity, charge, and biological specificity, respectively.

6.4 Technological Properties of Peptides from Protein-Rich Waste

Peptides differ from each other by the number of amino acids and the sequence of these molecules. Therefore, each peptide obtained from a different agro-industrial residue has its characteristics, such as color, flavor, emulsification, solubility, gelation, foaming capacity, and water and oil retention capacities. Such properties are often correlated with each other. It is known, for example, that the solubility of proteins is the precondition for some other functional properties, such as emulsification and foaming ability (Du et al. 2020).

Bioactive peptides are inactive within the basic structure of their parent proteins. To obtain these active peptides, it is necessary to carry out a hydrolysis reaction, which can be carried out using gastrointestinal digestive proteases or exogenous proteases (Mirzapour-Kouhdasht et al. 2021). Some peptides are found naturally, but most of them are synthesized from proteins using largely enzymatic, microbial, or chemical hydrolysis methods (Ashaolu et al. 2022).

Procedures for obtaining hydrolysates include their ability to denature, form new complexes, degrade amino acids, participate in Maillard reactions, and reduce amino acid digestibility. Therefore, the relationship between peptide quality and processing parameters can influence the functional performance of protein products. Many studies have carried out extensive investigations and attempted to modify plant proteins to improve their physical functionality (i.e., gelling, viscosity, emulsification, and foaming properties) (Coelho and de las Mercedes Salas-Mellado 2018).

One of the effects of protein hydrolysis is the change in functional properties compared to raw protein. The solubility, for example, of vegetable proteins, can be increased by hydrolysis. Surface hydrophobicity can also be improved through hydrolysis, revealing hydrophobic groups buried in the protein structure, thus increasing the oil-binding property and adsorption at the liquid-liquid or liquid-air interface, which consequently increases the ability to absorb water, emulsification, and foaming. Other altered technological properties are viscosity and oil- and water-holding capacities (Bozkurt et al. 2021).

Peptide solubility is strongly influenced by the amino acid composition and their sequence of amino acids, due to the polarity of the side chain. Therefore, peptides with a high content of hydrophobic residues, such as leucine, isoleucine, valine, methionine, phenylalanine, and tryptophan, will have limited solubility in an aqueous solution or will be completely insoluble (Sarma et al. 2018). Thus, for a food application, it is necessary to know the amino acid profile that constituted the peptide.

Sharma et al. (2022) investigated the solubility of protein hydrolysates obtained from corn distillery residues, to use them as additives for the storage of food products and as ingredients in animal feed. The authors verified that the insoluble proteins of the residues were converted into soluble peptides by enzymolysis, due to the creation of shorter peptides (higher solubility and lower viscosity) and the generation of carboxyl and amino groups.

To increase the solubility of peptides, as well as assist in the formation of emulsions, an alternative is the development of conjugates with polysaccharides. The polysaccharides that can be associated with peptides are chitosan, hyaluronic acid, cyclodextrin, agarose, starch, and cellulose, to form covalent bonds that increase solubility (Mohan et al. 2022).

Peptides generally have excellent emulsifying potential, which increases with increasing solubility. The stability of emulsions formed by peptides will depend on the amount of charge of the constituent amino acids (Du et al. 2022). In the development of emulsions with peptides, copolymers or other complexes are generally used. In addition to the emulsifying function, peptides are used in emulsions to increase emulsion stability and oxidative stability, promote antimicrobial and cryoprotective effects, and control lipid digestion (Ashaolu et al. 2022). In nanoemulsions, the use of food protein peptides as nanoemulsifying agents is limited, but there are already studies on the potential use of whey protein isolate hydrolysates as emulsifiers (Adjonu et al. 2014).

Whey has long been said to be a waste product from the dairy industry. However, many studies have found that whey contains several notoriously interesting remaining components, such as proteins, present in the form of a protein pool. These whey proteins have technological potential for the food industry, such as emulsifying, foaming, and gelling capacity, due to their excellent functional properties correlated with their physical, chemical, and structural characteristics. Bioactive peptides derived from milk proteins have attracted great interest because they are obtained through a low-cost and easily obtainable raw material, showing no toxicity and exhibiting different applications in foods (Yadav et al. 2015).

The emulsifying capacity of peptides depends on their characteristics, such as chain length/molecular size, conformation, hydrophilicity, and hydrophobicity. The molecular weight of peptides plays an important role in the formation and stabilization of emulsions, as it affects the adsorption at the oil-water interface and the nature of the interfacial layers formed (Adjonu et al. 2014).

Liu et al. (2022) showed the potential of using faba bean hydrolysates due to their excellent functional properties of solubility and emulsification. Although the authors carried out their studies on intact raw materials, obtaining hydrolysates from broken beans, which are unsuitable for commercialization, is an excellent option for using this product that would otherwise be discarded. Likewise, Felix et al. (2019) evaluated the emulsifying capacity of hydrolysates from chickpeas, obtained in their entirety, but could have been broken grains unsuitable for commercialization.

The ability of proteins and peptides to form gels is an important technological feature for application in foods. Gelation can be defined as the orderly aggregation of protein molecules denatured to a certain degree, thus forming a three-dimensional network that can absorb moisture, fat, sugar, and other flavor substances in food (Nafchi et al. 2013).

Gelation is a property of great importance when the peptides will be applied in dairy desserts, cooked meat products, and bakery products, among others. In addition, this property also influenced other technological properties, such as water absorption, emulsification, and foam formation and stabilization (Ordóñez 2005).

Different peptides, such as aliphatic, amphiphilic, and complementary ionic, are used as gelling agents to form low molecular weight hydrogels, to be used in delivery systems, protective agents for bioactive components, and a new food matrix (Du et al. 2022). Du et al. (2022) developed low molecular weight hydrogels using diphenylalanine and verified the use of solvent, pH, heating/cooling, enzymatic induction, and metal ion inducers in water and physiological buffer.

Foaming is the ability to incorporate air into a solution. The stability of the foam formed is a key parameter for the shelf life of foam-type foods. Once the foam is formed, it is necessary to maintain the desired appearance in the food and must maintain stability when subjected to a variety of processes, including mixing, cutting, and heating (Tang et al. 2021).

Tang et al. (2021) used peptides from different sources (soy, corn, whey, and fish skin) to aid in the foaming of egg whites. The authors found that, except for whey peptides, the addition of the other peptides increased foam formation, as well as increased foam stability. This positive effect may be due to the flexible molecular structures of the peptides, which can rapidly adsorb at the air-water interface during bubbling, undergo rapid conformation changes and rearrangement at the interface, and then form cohesive viscoelastic films through molecular interactions.

In addition to the stability of the peptide, the taste is another property evaluated for its application. Regarding taste, peptides are generally considered a barrier in their application in the food industry. Bitterness is presented by low molecular weight peptides, which contain hydrophobic amino acids such as leucine, proline, phenylalanine, and tyrosine. However, umami-tasting peptides are gaining more prominence (Zhang et al. 2022).

The ability of peptides to bind water and oil is very important in their application in foods, as they directly affect flavor, mouthfeel, and texture (Du et al. 2020). Pu et al. (2022) developed gel systems composed of whey peptides and egg white protein induced by cold acid. The authors found a water-holding capacity higher than 70%, increasing as the egg white protein content in the composite gels increased. Likewise, the parameters of hardness, adhesiveness, resilience, and gumminess of the composite gels increased significantly with increasing egg white protein. Regarding color, the gels became more yellow and harder, and the surfaces rougher with an increase in white protein.

The use of low-power high-frequency ultrasound in raw materials to obtain peptides has often been used as a pretreatment to produce bioactive peptides and therefore improve technological characteristics (Estivi et al. 2022). Associated with this, Mirzapour-Kouhdasht et al. (2021) evidenced the potential for obtaining bio-/multifunctional peptides derived from gelatin hydrolysates obtained from fish processing residues. These authors showed that, in addition to ultrasound, the use of pretreatments such as microwaves and high pressure to obtain peptides can improve technological properties. However, studies using physical and chemical pretreatments to obtain peptides focus only on bioactive and functional evaluation, not determining the technological characteristics.

6.5 Biological Properties of Peptides from Protein-Rich Waste

Proteins obtained from agro-industrial residues have proved to be an excellent raw material for obtaining bioactive peptides with potential for application in food, cosmetics, and pharmaceuticals (Tacias-Pascacio et al. 2021). In this sense, the study of biological properties in vitro and in vivo is an important tool to determine the effectiveness and relevance of bioactive peptides for human health (Daliri et al. 2017).

From a physiological point of view, the bioactivity of peptides is directly related to their bioavailability and bioaccessibility (Amigo and Hernández-Ledesma 2020). To promote beneficial effects on human health, bioactive peptides must go through different steps such as hydrolysis by digestive enzymes and blood proteases, which can generate new peptides with greater biological properties or inactivate peptide fragments (Chakrabarti et al. 2018).

The beneficial health effects of bioactive peptides are related to their ability to bind to physiological targets to carry out signaling processes that will be responsible for regulatory functions. Multiple factors such as molecular size, hydrophobicity, charge, and spatial conformation, offered by the variability of amino acid composition in their structure, have a direct effect on the wide range of biological effects of these molecules (Udenigwe et al. 2021).

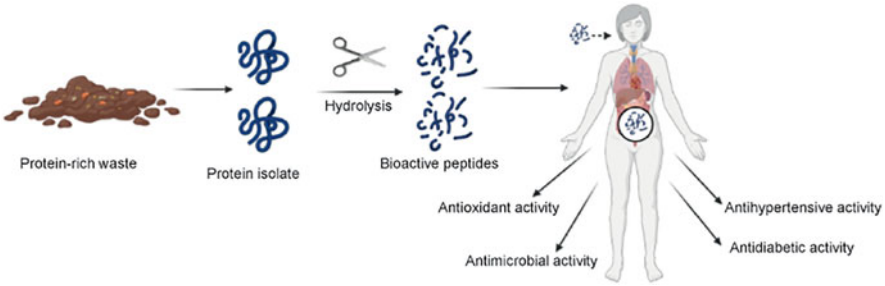

Fig. 6.2 An overview of the biological properties of bioactive peptides generated from protein-rich wastes

The bioactive peptides obtained from protein-rich residues may present several biological properties such as antimicrobial, antioxidant, antihypertensive, lipid regulation, and others (Fig. 6.2), demonstrated through in vitro and in vivo tests (Table 6.3).

The antioxidant capacity of bioactive peptides has been investigated almost exclusively through in vitro tests such as 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2-azino-bis(3-ethylbenzothiazo-6-sulfonic acid) (ABTS), ferric reducing antioxidant power (FRAP), oxygen radical absorbance capacity (ORAC), and others. Ryder et al. (2016) demonstrated that hydrolysis of connective tissue extract with HT protease resulted in peptides with antioxidant activity at the Trolox equivalence of 45 mmol L^{-1} using the ORAC assay. Oliveira Filho et al. (2021) reported that the enzymatic hydrolysis of proteins extracted from the cottonseed by-product by the microbial proteases Alcalase, Flavourzyme, and Neutrase generated peptides with antioxidant activity determined by the DPPH and FRAP methods. In another study, Fontoura et al. (2014) observed that peptides generated from feather proteins by fermentation with *Chryseobacterium* sp. kr6 showed higher antioxidant activity than the non-hydrolyzed protein extract using the DPPH and ABTS methods.

Studies have suggested that peptides with antioxidant activity can also act as ACE inhibitors, due to shared characteristics in terms of structure and size (Ryder et al. 2016). Ryder et al. (2016) observed that peptides generated from the hydrolysis of connective tissue extract with HT protease generated peptides with antioxidant and ACE inhibitory activity.

Angiotensin I-converting enzyme (ACE) inhibitor peptides are a class of bioactive peptides that have been commonly found originating from the hydrolysis of agro-industrial residues (Lemes et al. 2020a, b; Oliveira Filho et al. 2021; Ryder et al. 2016). ACE is responsible for catalyzing the proteolysis of the peptide angiotensin I to the peptide angiotensin II, a potent vasoconstrictor (He et al. 2013). Due to vasoconstriction caused by the production of angiotensin II, ACE has been reported to play a central role in hypertension (Becari et al. 2011). Fontoura et al. (2014) reported that the peptides generated from the hydrolysis of feathers obtained in 24 and 48 h of culture showed 53% and 65% of ACE inhibition, respectively. Oliveira Filho et al. (2021) observed that enzymatic hydrolysis of

Table 6.3 Biological properties of bioactive peptides generated from protein-rich wastes

Waste	Process	Biological activity	References
Residual proteins from the meat industry (myofibrillar and connective tissue)	Enzymatic hydrolysis (AFP, FPII, F31K, F60K, and HT)	Antioxidant and ACE inhibitory activities	Ryder et al. (2016)
Blood from deer, sheep, pigs, and cattle	Enzymatic hydrolysis (papain, bromelain, FP400, and FPII)	Antioxidant and antimicrobial activities	Bah et al. (2016)
Cottonseed meal	Enzymatic hydrolysis (Alcalase, Neutrase, and Flavourzyme)	Antimicrobial, antioxidant, and ACE inhibitory activities	Oliveira Filho et al. (2021)
Chicken feathers	Fermentation with *Chryseobacterium* sp. kr6	Antioxidant, ACE inhibitory, and dipeptidyl peptidase-IV inhibitory activities	Fontoura et al. (2014)
Chicken liver	Enzymatic hydrolysis (pepsin)	Antioxidant, anti-inflammation, and antifibrosis activities	Chen et al. (2017)
Viscera, head, tail, and fish structure	Fermentation with *Lactobacillus casei* (LC216, LC217, LC219, and LC220)	Antioxidant and antibacterial activities	Abd Rashid et al. (2022)
Torreya grandis bran	Enzymatic hydrolysis (Alcalase, Neutrase, pepsin, trypsin, and papain)	Antioxidant activity	Quan et al. (2021)
Liver	Enzymatic hydrolysis	Antidepressant effect	Nakagawasai et al. (2020)
Goat viscera	Enzymatic hydrolysis (Alcalase® and Brauzyn®)	Antioxidant activity	Queiroz et al. (2017)
Stems and leaves of cauliflower	Enzymatic hydrolysis (pepsin and pancreatin)	ACE inhibitory activity	Xu et al. (2016)
Chicken feathers	Fermentation with *Pedobacter* sp. 3.14.7	Antioxidant activity	Bezus et al. (2021)
Sunflower meal	Enzymatic hydrolysis (Alcalase and trypsin + chymotrypsin)	ACE and dipeptidyl peptidase-IV inhibitory activities	Şimşek (2022)

cottonseed by-product proteins generated peptides with 99% ACE inhibition. Xu et al. (2016) isolated the dipeptide (Val-Trp) from the protein hydrolyzate of cauliflower by-products and observed that this peptide has a potent ACE inhibitory activity with an IC50 of 31.30 μM.

Microbial resistance to synthetic antibiotics has attracted the attention of researchers and industry for natural antimicrobial compounds such as antimicrobial peptides. Antimicrobial peptides have several advantages over antibiotics, such as a wide range of antimicrobial activities including antifungal, antiviral, and

antibacterial, and because they do not contribute to the development of microbial resistance (Huan et al. 2020). Protein-rich residues have been considered attractive sources for the production of these molecules due to their low cost and high availability (Oliveira Filho et al. 2021). Bah et al. (2016) reported that peptides generated from the enzymatic hydrolysis of myofibrillar and connective tissue proteins by the fungal proteases FP400 and FPII were able to inhibit the growth of *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*. In another study, Abd Rashid et al. (2022) evaluated the antibacterial potential of peptides generated from the enzymatic hydrolysis of blood proteins from deer, sheep, pigs, and cattle. The authors reported that the peptides generated were able to inhibit the growth of *Listeria monocytogenes*, *Salmonella typhimurium*, *E. coli*, and *Listeria innocua*. Oliveira Filho et al. (2021) observed that the peptides generated through the hydrolysis of cottonseed by-product proteins with the enzyme Alcalase® were able to inhibit the growth of the bacterium *S. aureus* and the *Colletotrichum gloeosporioides* fungus.

Dipeptidyl peptidase-IV (DPP-IV) enzyme inhibitors have emerged as a new class of substances for the treatment of type 2 diabetes, as this enzyme rapidly degrades glucagon-like peptide 1, a hormone that normalizes glucose concentration in the blood (Green et al. 2006). Fontoura et al. (2014) demonstrated that chicken feather hydrolysates were shown to inhibit the DPP-IV enzyme by 44%. In another study, Şimşek (2022) reported that the fraction of peptides generated by the hydrolysis of sunflower bran proteins that have a molecular weight of less than 5 kDa showed the most potent inhibitory capacity of the DPP-IV enzyme with an IC_{50} of 0.30 mg/mL.

In addition to the above activities related to antioxidant, antihypertensive, antimicrobial, and antidiabetic effects, peptides obtained from protein-rich residues may also exhibit antidepressant, hepatoprotective, and other properties (Nakagawasai et al. 2020). Peptides generated after liver hydrolysis showed an antidepressant effect in olfactory bulbectomized mice by increasing hippocampal AMPK-phosphate, cyclic adenosine monophosphate response element binding protein, and brain-derived neurotrophic factor (Nakagawasai et al. 2020). In another study, peptides obtained after hydrolysis of chicken liver proteins showed a hepatoprotective effect by upregulating transforming growth factor beta (TGF-β) and SMAD family member 4 (SMAD4) caused by thioacetamide-induced liver fibrosis in rats (Chen et al. 2017).

The peptides generated from the proteins of agro-industrial residues have a wide spectrum of biological properties that make them promising biomolecules in the development of drugs, functional ingredients for food, cosmetics, and others.

6.6 Conclusion

Waste, both from animal and plant sources, can be a viable source of raw protein for the production of bioactive peptides, since they are produced in large quantities, are usually used in animal feed or fertilization, and are therefore usually economically

devalued. Bioactive peptides can contribute to the technological properties of food products such as solubility and gel and emulsion formation, among others. Furthermore, chemical, enzymatic, and/or microbiological processes seem to be an interesting alternative for the production of bioactive peptides with biological properties that improve human health. In this way, the production of bioactive peptides, in addition to increasing the added value of the waste generated by agro-industries, is also an important ingredient that can be used in the pharmaceutical or food industries.

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Chapter 7
Biopolymers in Sugarcane Vinasse Treatment and Valorization

M. A. da Silva, R. G. Bastos, M. R. Soares, B. C. Cerri, S. R. Bettani, G. C. de Jesus, G. O. Ragazzo, and N. L. Santos

Abstract The rise in global population and industrialization reflects the increase in energy consumption. Fossil fuel still represents the major energy resource, but its non-renewable nature and the environmental impacts caused by its use have forced governments and industries to search for alternative energy sources, including ethanol. Sugarcane is the second most used feedstock for ethanol fuel production, accounting for 22% of global ethanol estimated at 27 billion L per year. Vinasse, a highly polluting nutrient-rich dark liquid, is the most expressive wastewater from this sector generated in huge volumes (10–14 L/L of ethanol). Fertigation has been its main destination; however, concerns about the harmful effects on soil and groundwater caused by nutrient lixiviation have increased the interest in innovative alternatives for the use and treatment of vinasse. This chapter discusses the potentialities of associating biopolymers with the treatment and valorization of this wastewater focusing on the sustainability of the process and generation of high-added value products.

Keywords Sugarcane vinasse · Ethanol · Biopolymers · Microalgae immobilization · Soil fertilizers · Mulching

7.1 Introduction

Vinasse is the main wastewater from sugarcane processing, generated from the fermentation-distillation process of sugarcane juice, molasses, or their mixtures. Current production technologies result in 10–14 L of vinasse for each liter of ethanol, suggesting a generation of more than 320 billion L of vinasse per crop season in Brazil. As direct disposal of this wastewater in water bodies is prohibited

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and fertigation is limited by vinasse and soil chemical characteristics, as well as economic distance for transportation, new technologies aiming at more sustainable use of vinasse become necessary and have been the subject of several research studies. Regarding the treatment of vinasse in terms of removing its pollutants, the immobilization of microalgae in biopolymeric matrices is an alternative to designing viable continuous processes, with the generation of biomass and the obtaining of intracellular components and value-added metabolites. Considering that the most common use of this wastewater is in the fertigation of sugarcane crops, obtaining slow-release biodegradable fertilizers based on biopolymers and vinasse could make this application even more viable, allowing its transport beyond economic distances and hinder ion lixiviation that can lead to groundwater contamination among other environmental impacts. In addition, biodegradable mulching films enriched with vinasse represent another alternative to vinasse use and disposal, favoring agricultural cultures in several aspects. This chapter provides an overview of aspects related to the application of biopolymers in sugarcane vinasse treatment and valorization, mainly presenting potential technologies to be explored in the areas of Biotechnology and Agronomy.

7.2 Ethanol Production

The increasing demand for alternative and cleaner energy sources has boosted the worldwide interest in ethanol. It has been used for more than 50 years and is considered one of the more important and sustainable biofuels (Bergmann et al. 2018; Fito et al. 2019; Fuess et al. 2017). Several biomasses can be used for ethanol production including those based on sucrose (sugarcane, sugar beet, and sweet sorghum), starch (maize, cassava, rice, and wheat), and cellulose material (bagasse, straw, and wood) (Joshi et al. 2020; Bajpai 2021). However, due to raw material availability and technological developments, the great majority of bioethanol produced in the world comes from maize and sugarcane, about 59 and 22%, respectively (OECD/FAO 2022). Figure 7.1 illustrates the main producing countries and the feedstocks used for ethanol production. The United States and Brazil lead world production, responding for 73% of total average production 2019–2021 (124.7 billion L), followed by China (8.4%), India (2.9%), Canada (1.6%), and Thailand (1.4%).

Albeit the major global ethanol production is based on maize, ethanol from sugarcane has attracted worldwide importance and is used in many countries, including Brazil. Sugarcane exhibits higher ethanol productivity compared to maize, yielding 5–10.8 m^3/ha, compared to 2–4.6 m^3/ha from maize, and also lower emission of greenhouse gases (GHG) (Manochio et al. 2017). Brazil is the largest sugarcane producer, harvesting 654 million tons in season 2020/2021, cultivated in approximately 8.6 million ha of planted area (CONAB 2022). Energy from sugarcane biomass is the main source of renewable energy in Brazil, representing 19.1% of the national energy matrix (ENE 2021). The ethanol demand

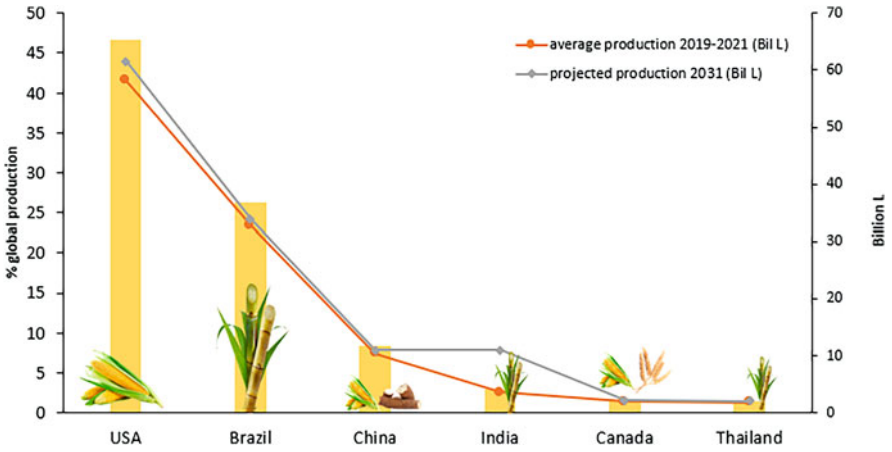

Fig. 7.1 Ethanol production by main producing countries and main feedstock used: market share (% average 2019–2021, left axis, bars) and production in volume (average 2019–2021 and projected for 2031, rigth axis, lines) (OECD/FAO 2022)

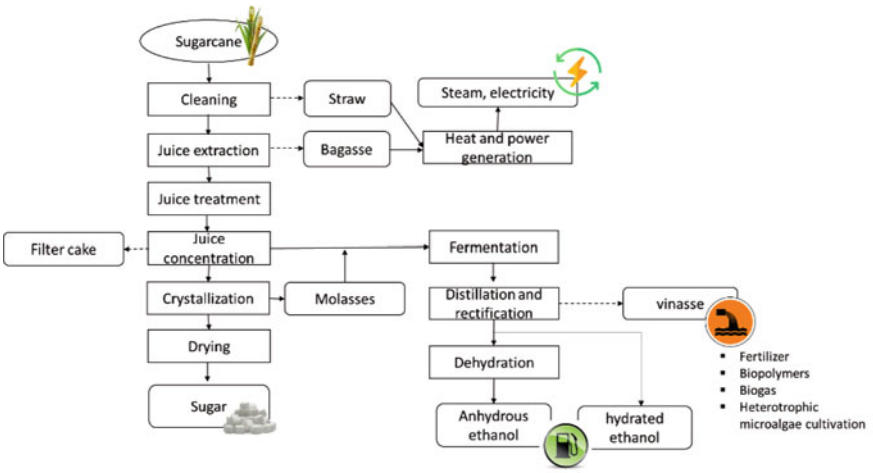

Fig. 7.2 Simplified flowchart of sugarcane ethanol and sugar production process

in Brazil is expected to grow in the next years following the country's commitments made at the United Nations Climate Conference (COP21). A recently launched biofuel program, named RenovaBio, expects to reduce over 10% of GHG emissions of the transport energy matrix by 2028.

Typically, sugarcane mills work as integrated systems producing both ethanol and sugar, the so-called annexed sugarcane mills (Bastos et al. 2022; de Souza Dias et al. 2015). A typical scheme of sugarcane first-generation ethanol and sugar industry is presented in Fig. 7.2. The industrial process of ethanol and sugar

production starts with the reception of the mechanically harvested sugarcane, cleaning, and juice extraction. This later process takes place in mills, usually by soaking with water to recover the maximum sucrose. The sugarcane juice is then treated to remove impurities and reduce contamination by sieving, liming to adjust pH to 5.6–5.8, heating, flocculating, concentration to 50–60° Brix, and cooling. After crystallization for sugar production, a concentrated residual solution is obtained (molasses). Molasses and sugarcane juice are blended for yeast fermentation (usually 6–12 h in fed-batch fermenters using *Saccharomyces cerevisiae* recovered from a previous cycle) and the resulting ethanolic product (7–12°GL), called wine, goes to distillation and dehydration to produce anhydrous ethanol (Lopes et al. 2016) producing vinasse as a by-product (Bergmann et al. 2018). Steam and electricity used in the process come from sugarcane bagasse and straw as fuel, and exceeding power is sold to the grid. Bagasse and straw have attracted increasing interest aiming the production of second-generation ethanol.

7.3 Sugarcane Vinasse

Sugarcane vinasse, also called stillage or distillery spent wash, is a high pollutant liquid residue from the ethanolic fermentation-distillation process of sugarcane juice, molasses, or its mixtures (Fito et al. 2019). It represents the most expressive wastewater, in terms of quality and quantity, from the sugar and ethanol industries. Current production technologies result in 10–14 L of vinasse for each liter of ethanol (M da Silva et al. 2007; Fito et al. 2019; Trevisan et al. 2020). So, taking into account that the Brazilian total ethanol production in 2021/2022 was about 32 billion L (CONAB 2022), more than 320 billion L of vinasse were generated.

This wastewater has a typical strong unpleasant odor, dark-brown color, low pH (3.7–4.5), high contents of suspended solids, organic, and inorganic compounds, and high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Bastos et al. 2022; Brasil et al. 2017). There is no conventional treatment for vinasse capable of reaching legal standards to allow its release directly into water bodies. In Brazil, the direct discharge of vinasse in the water bodies close to the refinery was historically a common practice until it was prohibited in 1980 (BRASIL 1980). Since then, fertigation of sugarcane crops which comprises the application of non-treated vinasse in the soil is pointed out as the main solution for vinasse disposal, and the sugar and ethanol sector has been managing to partially neutralize the pollution potential of vinasse's high organic load through this practice (Christofoletti et al. 2013).

When applied in the soil it can enhance fertility and soil characteristics, reduce inorganic fertilization, and thus benefit agricultural cultures. However, the application rate of vinasse in fertigation depends not only on the characteristics of vinasse but also on soil and culture (mostly sugarcane crops near the processing unity) and should not exceed the ion retention capacity in the effective absorption root absorption zone (up to 0.8 m depth of soil profile). Overdosed vinasse applications can

result in ion lixiviation, especially nitrate (NO_3^-) and potassium (K^+), which can affect adjacent areas and groundwater causing environmental and sanitary impacts. Other potential impacts associated with fertigation include soil salinization, organic overloading, overfertilization, and soil acidification (Fuess et al. 2017). In Brazil, the application dosages are established by legal limits according to the technical normative P4.231 (CETESB 2015) which has allowed 150 m^3 ha^{-1} on average. The calculation depends on the potassium content and cation exchange capacity (CEC) of the soil (up to 0.8 m depth) and the K_2O content of vinasse. Despite being considered a great advance in terms of environmental legislation, the normative has been criticized as the dosage of other compounds such as nitrates, sulfates, and organic matter is not controlled by the calculation and therefore may trigger significant environmental negative effects (Fuess et al. 2017).

Vinasse, as a liquid, is mostly composed of water (about 93%), and therefore its application in areas far from the distillery can be limited by high costs of transportation. The transportation of vinasse to the field (either by trucks or pipelines) is strictly dependent on the balance between transportation and mineral fertilization costs, to achieve an economic distance beyond which fertigation becomes unfeasible. So, the sugarcane areas near the refineries may become insufficient to absorb the actual volumes of vinasse and attend to legislation standards. Repetitive applications can increase the risk of soil saturation, unchaining negative impacts of its use such as soil nutrient unbalance, groundwater contamination, unpleasant odor intensification, and insect vector proliferation (Parsaee et al. 2019). For those reasons, vinasse disposal has become one of the greatest challenges in the sector. Consequently, alternative technologies for the use of this residue have been proposed, including biodigestion to produce biogas, aerobic and anaerobic treatment, use as a growth medium for the production of unicellular protein, use in animal feed, and concentration by evaporation (Christofoletti et al. 2013; Parsaee et al. 2019).

The use of concentrated vinasse has been considered a feasible way to vinasse application beyond the maximum economic distance. Besides the reduction of transportation costs, the concentrated vinasse can dispense sprinkling, and depending on its concentration its application can be done through distribution in the line as conventional solid fertilizers.

Concentration by evaporation demands high energy inputs, so alternative concentration methods have been studied, such as membrane separation methods. Nataraj et al. (2006) described a hybrid nanofiltration and reverse osmosis process to concentrate and remove color and contaminants from vinasse.

Anaerobic digestion has been proven to successfully reduce the levels of organic matter, and produce biogas (Parsaee et al. 2019). However, other processes are needed to further reduce levels of organic and inorganic components. These can include common physicochemical processes such as flocculation and/or adsorption; however other advanced technologies such as electrocoagulation, ultrafiltration, and ozone treatment have been proposed (Fuess et al. 2017; Montaño et al. 2019; Moraes et al. 2015; Reis Cristiano et al. 2019).

Novel alternative solutions for the production of high-added value products from vinasse, such as protein, lipids, enzymes, and other organic compounds, have also

been gaining increasing attention (Fernandes et al. 2017). Vinasse is also proposed as a substrate for heterotrophic cultivation of microalgae, and the production of biopolymers and lignocellulosic material (da Silva et al. 2017; de Jesus et al. 2019; de Mattos and Bastos 2016; Marques et al. 2013; Naspolini et al. 2017; Reis Cristiano and Hu 2017; Santana et al. 2017). Microalgae cultivation in vinasse promotes the removal of organic matter, color, and nutrients upgrading the wastewater for fertigation (de Mattos and Bastos 2016).

7.4 Physicochemical Characteristics of Sugarcane Vinasse

Assessment of the inorganic and organic composition of vinasse and its variation is of great interest to industry and academy to conduct research and propose innovative alternatives for sugarcane vinasse use and disposal (de Godoi et al. 2019). The physicochemical characteristics of vinasse are variable and depend on raw material (sugarcane variety and maturation), most preparation (sugarcane juice, molasses, or blends), fermentation method, and distillation (España-Gamboa et al. 2011). The feedstock planting system, soil management, and use of fertilizers can affect vinasse composition. Sugarcane juice treatment processes, such as sulfitation, can enrich the most with sulfur compounds, especially sulfate species (Della-Bianca et al. 2013). de Godoi et al. (2019) evaluated the seasonal variation of the sugarcane vinasse composition throughout the harvesting season and among three harvesting seasons (2015–2017) of one annexed sugar-ethanol refinery in Brazil. These authors concluded that sugarcane crop cultivation and the processing parameters were the main factors influencing vinasse characteristics.

Table 7.1 shows the average composition of sugarcane untreated vinasse (Bettani et al. 2019; Candido et al. 2021; de Godoi et al. 2019; de Mattos and Bastos 2016; Fuess et al. 2017, 2018; Morais and Bastos 2019; Naspolini et al. 2017; Reis Cristiano et al. 2019). Sugarcane vinasse shows a high organic load with high levels of BOD (14.4–27 g L^{-1}) and COD (22.9–51.8 g L^{-1}) accounting for the high polluting potential of this wastewater. It also contains primary ($N\text{-}NO_3^-$, $N\text{-}NH_4^+$, and mainly K^+) and secondary (Ca^{2+}, Mg^{2+}, and SO_4^{2-}) macronutrients, and micronutrients (Cu^{2+}, Fe^{2+}, Mn^{2+}, and Zn^{2+}) (Morais and Bastos 2019).

The acidic nature of sugarcane vinasse is related to the fermentation step as biotransformation of sugar to alcohol occurs in acidic conditions to hinder bacterial contamination. It is also attributed to non-*Saccharomyces* yeast and bacteria metabolites such as organic acids (Lopes et al. 2016).

Potassium, calcium, and magnesium are the major ions in vinasse originating from sugarcane crops and juice extraction (Fuess et al. 2018). Potassium is the most absorbed nutrient during sugarcane plant growth highlighting the importance of vinasse as a fertilizer leading to recycling water and nutrients. However, potassium and sodium cations can promote the dispersion of clay particles, decreasing soil porosity and thus its permeability and loss of microbial activity (Mutton et al. 2014).

Table 7.1 Physicochemical attributes of raw sugarcane vinasse

Parameter	Range[a]
pH	3.9–4.9
Temperature at the bottom of the distillation column (°C)	80–100
BOD (g L^{-1} O_2)	14.4–27.0
COD (g L^{-1} O_2)	22.9–51.8
Total solids (g L^{-1})	23.7–45.9
Total organic carbon (g L^{-1} °C)	5.7–17.4
Nitrogen (mg L^{-1} N)	119–1404
Phosphorus (mg L^{-1} P)	25.6–232
Potassium (mg L^{-1} K)	1330–4340
Calcium (mg L^{-1} Ca)	292–2240
Magnesium (mg L^{-1} Mg)	102–669
Sulfate (mg L^{-1} SO_4^{-2})	918–3800
Iron (mg L^{-1} Fe)	5.7–18.7
Copper (mg L^{-1} Cu)	0.13–1.16
Zinc (mg L^{-1} Zn)	0.25–1.29
Manganese (mg L^{-1} Mn)	1.01–4.62

[a]Bettani et al. 2019; Candido et al. 2021; de Godoi et al. 2019; de Mattos and Bastos 2016; Fuess et al. 2017, 2018; Morais and Bastos 2019; Naspolini et al. 2017; Reis Cristiano et al. 2019

A wide variety of organic compounds have also been identified in vinasse samples, such as alcohols, aldehydes, ketone, esters, acids, and sugars. These compounds can come from raw material or be produced by thermal degradation during fermentation and distillation. Glycerol, lactic acid, and sorbitol are usually present, and their market value can boost the search for extraction routes to residue valorization (Carrilho et al. 2016; Reis Cristiano and Hu 2017).

Highly colored compounds found in vinasse can reduce light penetration and therefore photosynthetic activity in aquatic environments (Prasad et al. 2008). Some phytotoxic, antibacterial, and recalcitrant compounds such as phenols, polyphenols, melanoidins, furfurals, and heavy metals are also present (Johnson et al. 2019).

7.5 Use of Biopolymers in Sugarcane Vinasse Treatment and Valorization

7.5.1 Microalgae Immobilization in Biopolymeric Matrices for Vinasse Treatment and Biomass Accumulation

Owned to its chemical composition, rich in organic and inorganic compounds, vinasse can be considered an attractive nutritive growth medium for microorganisms under anaerobic and aerobic conditions, allowing treatment and production of high-added value biomass. Several studies using bacteria, yeast, and/or microalgae have

been conducted to attempt alternative treatments to vinasse showing economical and environmentally friendly possibilities. Kaushik and Thakur (2009) investigated the process of vinasse treatment using selected *Bacillus* sp. strains. Under optimized conditions, the bacteria were able efficiently to treat the wastewater achieving 85% of color and 90% COD removal within 12 h. Another study demonstrated promising results by substituting water with vinasse in the alcoholic fermentation medium with *Saccharomyces cerevisiae* CMI237 (Navarro et al. 2000). In recent work, Ahmed et al. (2022) studied the treatment of vinasse by *Trametes* sp. strain immobilized in polyurethane foam. The authors reported the treated vinasse showed decreased levels of COD, BOD, color, total phenolic compounds, and phytotoxicity, while the fungus produced a considerable amount of laccase a high value-added product.

Microalgae are a group of distinct microorganisms, including eukaryote photosynthetic organisms, such as chlorophyceae algae (Chlorophyta), as well as prokaryote organisms, such as cyanobacteria (Cyanophyceae) (Mata et al. 2010). The classification of microalga has traditionally been made based on the type of pigment, chemical nature of reserve products, cell wall constitution, and also cytological and morphological criteria. They are naturally found in aquatic/moist environments, such as rivers, lakes, oceans, and soils (Andrade et al. 2020; Tomaselli 2003).

Microalgae are considered strategic biotechnological resources, own to their ability to grow fast and in a wide range of environments, including several industrial wastewaters, simultaneously providing remediation with nutrient accumulation and production of useful biomass (Johnson et al. 2019). A wide range of products and high-added value bioactive compounds can be obtained, such as proteins, lipids, carbohydrates, pigments, vitamins, and sterols for applications in different industrial segments such as bioenergy, food/feed, and pharmaceutical. In some cases, microalgal biomass can be produced using agro-industry by-products or residues, as a biorefinery (Andrade et al. 2020; Brasil et al. 2017). Compared to land crops biomass, microalgae biomass has some considerable advantages, which include productivities 10–100-folds higher, high ability to capture carbon dioxide, high carbohydrate, and lipid content, ability to grow in seawater, and wastewater, and do not need arable land to grow. Besides, microalgae can be harvested continuously throughout the year, so allowing continuous production of biofuels and other products (Brasil et al. 2017; Marques et al. 2013).

Microalgae are usually cultivated under photoautotrophic conditions, through photosynthetic metabolism capturing energy from light (natural or artificial) and fixing inorganic carbon from CO_2. However, several microalgae species can grow under heterotrophic conditions, i.e., in the absence of light using organic carbon compounds as energy and carbon sources. Mixotrophic cultivation is also possible when microalgae species undergo combined photoautotrophic and heterotrophic metabolisms using organic and inorganic carbon sources in the presence of light (Wang et al. 2014). Heterotrophic growth is possible inside opaque fermenters and tends to achieve higher productivities than photoautotrophic and mixotrophic cultivations. Another advantage is that as growth is not light-dependent, its rate is not affected by changes in medium turbidity, so higher cell densities can be achieved and also allow its cultivation on dark wastewater such as vinasse (Brasil et al. 2017; de

Mattos and Bastos 2016; Reis Cristiano and Hu 2017). On the other hand, substrates costs and contamination are important issues to consider for heterotrophic microalgae cultivation. Contamination control can be even more challenging for large-scale microalgae cultivation if the use of waste streams rich in organic compounds is considered (Marques et al. 2013).

Vinasse contains organic carbon, nitrogen, potassium and phosphorus, calcium, magnesium, iron, and manganese, among other nutrients available in sufficient amounts to sustain microalgae growth. Its use as a growth medium for microalgae biomass production was first proposed by Oliveira and Cáceres (1986), who used diluted vinasse for the cultivation of *Chlorella vulgaris* CCAP-211/11b. These authors verified that mixotrophic growth was similar to photosynthetic growth, and an accumulation of carbohydrates by cells in heterotrophic conditions. de Mattos and Bastos (2016) obtained removals of 36.2% and 52.1% of COD and total nitrogen in 30 h, respectively, by heterotrophic cultivation of *Desmodesmus* sp. in sugarcane vinasse. Morais and Bastos (2019) used sugarcane vinasse to complement the microbial medium for the cyanobacterium *Aphanothece microscopic* Nägeli aiming at the production of the "blue pigment" phycocyanin. Montaño et al. (2019) evaluated the growth of the green microalgae *Desmodesmus subspicatus* and nutrient removal from vinasse after pretreatment by electrocoagulation. The authors reported that the pretreatment facilitated growth due to the removal of turbidity and pH neutralization of the vinasse, obtaining removals of 66 and 75% of initial total organic carbon and total nitrogen, respectively, with biomass productivity of 1.45 g L^{-1} day^{-1} and maximum specific growth rate of 0.095 h^{-1}. Bastos et al. (2022) discussed the challenges associated with the scale-up of the production of microalgal biomass from sugarcane vinasse. The authors highlighted that the main bottleneck for heterotrophic microalgal growth and extending to any scale of cultivation is bacterial contamination, which could affect the composition of the generated biomass and its final applications. *Spirulina maxima* demonstrated higher biomass productivity and protein content when grown under cycled light-autotrophic/dark-heterotrophic conditions in a medium added with sugarcane vinasse (dos Santos et al. 2016).

After cultivation, the algal biomass must be harvested to separate the biomass from treated water. The small size of single cells makes harvesting one of the major practical limitations for the development of microalgae-based wastewater treatment systems and can be responsible for up to 30% of the total production costs. It usually involves one or more steps of flocculation, filtration, flotation, settling, and/or centrifugation (Brasil et al. 2017; Moreno-Garrido 2008).

Cell immobilization techniques are suggested to overcome those problems. Immobilization of microalgae, following the trend for other microorganisms, has been widely used for biotechnological applications focusing on biomass production and nutrients/pollutants removal (De-Bashan and Bashan 2010). It consists in confining the cells in a physical structure and so keeping them in a specific region of the bioreactor.

These systems have some advantages compared to free cell cultivation, such as maintenance of high cell concentrations, high substrate to product conversion rates,

facilitated cultivation, and biomass harvesting. Moreover, immobilization may increase cell tolerance to adverse environmental conditions (temperature, acidity, toxicants), enhance biosorption, and allow continuous system operations (de Jesus et al. 2019; Eroglu et al. 2015). Cell immobilization can be achieved by different techniques including adsorption, covalent coupling, liquid-liquid emulsion, capture on a semipermeable membrane, and polymer gel entrapment. Most commonly, microalgae immobilization is attained by entrapment in a gel matrix made from synthetic polymers (acrylamide, polyurethanes, polyvinyl, polystyrene) and biobased polymers (alginate, carrageenan, pectin, agar, chitosan, gelatin, albumin) (Caldwell et al. 2021; De-Bashan and Bashan 2010). Synthetic polymers usually exhibit greater matrix resistance; however, natural matrices usually provide better diffusion nutrient and product rates and do not impose environmental problems associated with plastic accumulation. Some criteria to be considered for choosing an entrapment material are low solubility, high mechanical stability, high diffusivity, high cell retention efficiency, simple preparation, and low cost (Leenen et al. 1996). Chevalier and de La Noüe (1985) were pioneers in microalgae immobilization, producing *carrageenan-based* beads containing immobilized *Scenedesmus obliquus* for the removal of nitrogen and phosphorus from wastewater of Valcartier military base in Canada.

Among biopolymers, alginate has been one of the most used biopolymers for microalgae immobilization. Sodium alginate is an anionic polysaccharide extracted from different species of brown algae. Chemically it is composed of linear chains of (1–4)-linked-β-D-mannuronic (M) and α-L-guluronic (G) acids linked by (1–4) covalent bonds. The acid residues are arranged in blocks of consecutive MM or GG blocks or alternated sequences (MG) along the polymer chains. Adjacent carboxylic groups on alginate chains can react with divalent ions, such as calcium (Ca^{2+}) forming strong water insoluble three-dimensional structures. The mechanism of calcium alginate formation is known as the "egg-box" model (Bierhalz et al. 2014; de Jesus et al. 2019).

Alginate beads are non-toxic, transparent, permeable, relatively low cost (compared to other matrix biopolymers), prepared under mild conditions, and capable of maintaining microalgae viability for long periods. In sugarcane vinasse or other nutrient-rich wastewater treatment, the alginate beads could be collected, dried, and applied as soil fertilizer enhancing the sustainability of the production chain (Bettani et al. 2019). On the other hand, alginate is unstable in the presence of chelating and antigelling ions such as phosphate and citrate ions, usually present in wastewater, which can lead to bead disruption and dissolution (Jiménez-Pérez et al. 2004; Soo et al. 2017). So, understanding the parameters affecting bead stability is essential to enhance wastewater treatment performance. The gel strength and solubility are dependent on the proportion of the GG, MM, and MG blocks, as well as on the polymer concentration and molecular weight, type and concentration of the crosslinking agent, and preparation methods (Voo et al. 2016).

de Jesus et al. (2019) studied the preparation method of alginate beads for immobilization of *D. subspicatus* (Fig. 7.3). These green microalgae are naturally found in freshwater, especially in nutrient-rich environments. They have been

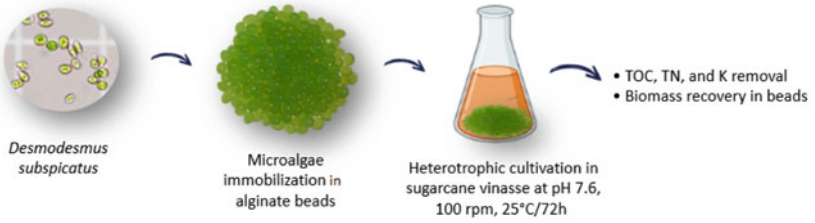

Fig. 7.3 Simplified scheme of immobilized *Desmodesmus subspicatus* heterotrophic cultivation in sugarcane vinasse

cultivated as free and immobilized cells in industrial, domestic, and synthetic wastewater exhibiting high cell viability, acidic tolerance, and temperature (da Silva et al. 2017). Alginate (1, 2, and 3% w/v) and crosslinking agent (2, 5, and 10% w/v $CaCl_2$) concentrations were tested. The beads showed good stability in vinasse, BG11 medium, and distilled water with no bead dissolution after 7 days at 25 °C. Interestingly, alginate beads in contact with vinasse were more stable compared to other media, indicating that the high concentration of calcium in the wastewater enhanced crosslinking level and hence bead stabilization. The presence of microalgae did not affect the diameter and compression force of beads, compared to blank beads (without microalgae). Increasing alginate concentration from 1 to 2% w/v regardless of the crosslinking agent concentration resulted in more strengthened, spherical, and uniform beads. Free and immobilized *D. subspicatus* in alginate beads were cultivated in sugarcane vinasse under heterotrophic conditions for 72 h at 25 °C. Free and immobilized microalgae (alginate 2% w/v crosslinked with 5% $CaCl_2$) decreased the levels of TOC, TN, and K by 45, 49, and 8% and 38, 27, and 28%, respectively. The lower TOC and TN uptake for immobilized microalgae is probably related to diffusion restrictions, also evidenced by the lower growth rate. Blank alginate beads showed significant K uptake, indicating additional removal by adsorption in the polymeric matrix increasing the potential of using immobilized systems for vinasse treatment (de Jesus et al. 2019).

7.5.2 *Slow-Release Biodegradable Fertilizers Based on Biopolymers and Vinasse*

The increasing global demand for water, food, and energy will undoubtedly urge great governmental, academic, and producers' efforts to develop more sustainable production systems capable of providing food and environmental security (Calabi-Floody et al. 2018). So, alternative and novel technologies for agriculture are at the

center of these issues as a key to avoid future problems. These include more efficient and less aggressive use of fertilizers and pesticides, adequate and reuse of agricultural by-products and wastes, alternative energy sources, and improved water management.

Duhan et al. (2017) report that about 40–70% of N, 80–90% of P, and 50–70% of K from fertilizers are lost to the environment causing enormous economic and environmental impacts. One of the most promising strategies is the development of slow/controlled release fertilizers which can be combined with other active components such as enzymes and microorganisms (Rashid et al. 2021). These systems, also known as enhanced efficiency fertilizers, allow the reduction of the applied quantity of fertilizers by exhibiting release patterns more compatible with the crop cycle. The most used mechanisms to achieve slow/controlled release fertilizers include the use of materials that hinder nutrient solubility, coating the mineral fertilizer to avoid rapid release, and restricting the surface-to-volume ratio of the material.

A great variety of synthetic and semisynthetic non-biodegradable polymers were proposed and used for coating mineral fertilizers such as polyurethanes, polyacrylamide, poly(*acrylamide*/sodium *acrylate*), *polyacrylonitrile*, and *polystyrene (*Cerri et al. 2020*;* Zhong et al. 2013*). However, these materials usually need harmful solvents, and most of them lead to plastic residue accumulation in soil estimated at* up to 50 kg/ha/year (Fertahi et al. 2021; Rozo et al. 2019). To overcome these drawbacks, a crescent interest in biobased materials has arisen; these are usually cheaper, biodegradable, non-toxic, and can enhance soil properties and water holding capacity (Bettani et al. 2019; Fertahi et al. 2021; Zhong et al. 2013).

The most common biopolymers used for slow/controlled release fertilizer applications are starch, alginate, pectin, carrageen, cellulose, chitosan, and guar gum. Biopolymers are usually hydrophilic and have limited mechanical resistance compared to synthetic ones, so to overcome these drawbacks chemical and physical modifications can be needed, such as the use of crosslinkers and plasticizers, blending with other biopolymers, and the addition of reinforcement nanomaterials (Fertahi et al. 2021).

Pectins are complex anionic polysaccharides mainly derived from agro-by-products such as apple pomace and citrus bagasse. Pectin chains are formed by α-(1,4)-liked-galacturonic acid residues which are partly methyl esterified depending on the source and method of extraction. The degree of esterification (DE) determines the gelation mechanism and gel properties being classified as low methoxyl pectins (LM, DE $<$ 50%) or high methoxyl pectins (HM, DE $>$ 50%). LM pectins tend to form strong gels by interaction with divalent cations described by the "egg-box" model, similar to alginate (Fang et al. 2008), whereas in HM pectins hydrogen bonds and hydrophobic forces predominate and gel formation occurs under acidic conditions (pH $<$3.5) and high soluble solids content (Gawkowska et al. 2018).

Another promising biopolymer is chitosan, obtained by deacetylation of chitin. Chitosan is an anionic copolymer consisting of D-glucosamine and N-acetyl-D-glucosamine units, linked by β-(1,4) bonds (Michalik and Wandzik 2020). The molecular weight and the degree of acetylation (DA) are the main characteristics

that affect the properties of chitosan gels. Chitosan is insoluble in water but is soluble in weak acid solutions by protonation of the amino groups. Chitosan can show inherent antimicrobial properties which could enhance its benefits in agricultural applications.

Some characteristics of vinasse, such as low pH, high soluble solids, and calcium content (de Godoi et al. 2019; Navarro et al. 2000), make it an appealing liquid media for pectin and chitosan gel formation expanding the alternatives for vinasse disposal and use as a slow release fertilizer. Bettani et al. (2019) investigated the process of formation of biodegradable particulate fertilizers based on pectin and sugarcane vinasse by a simple dripping crosslinking technique. Raw vinasse served as the solvent for the biopolymer providing HM pectin gel formation and stability, as well as acting as a nutrient source. The chemical composition of the dry particles indicated high concentrations of N, K, Ca, Mg, and micronutrients. Besides, the incorporation of lipid extracted microalgae (*D. subspicatus*) biomass residue (LMBR) in the fertilizer formulation enhanced nutrient content and can be integrated, along with vinasse, in a biorefinery concept. Compared to fertigation, vinasse-enriched solid particles offer a novel and more efficient way of fertilization and wastewater disposal. The dry particles can be more easily transported and therefore be applied to agricultural cultures beyond sugarcane crops near the distilleries.

In another study of the same research group, Cerri et al. (2020) characterized and evaluated the water retention properties of vinasse-added pectin and chitosan slow-release particles (Fig. 7.4). Similar to the previous work, stable solid particles were obtained with great retention of vinasse nutrients in the dry particles. Chitosan/vinasse particles exhibit higher mechanical and water resistance compared to pectin/vinasse particles. Both particles were able to retard the water evaporation rate from sandy soil representing an additional feature of these fertilizers.

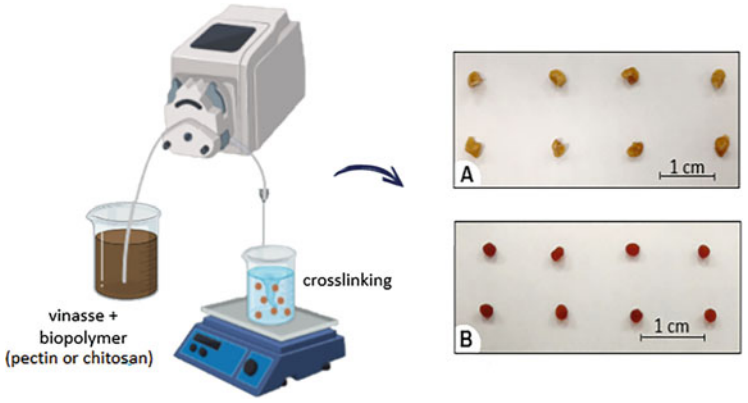

Fig. 7.4 Preparation of biodegradable particulate fertilizers and visual aspect of the pectin/vinasse (**a**) and chitosan/vinasse (**b**) particles

7.5.3 *Biodegradable Mulching Films Enriched with Vinasse*

The great versatility and relatively low cost of synthetic plastic materials reflect their widespread use for many applications including in agriculture for greenhouse covers, mulches, low tunnel films, drip irrigation tape, plant containers, nets, silage bags, trays, seedling bags, and seed tapes (Adhikari et al. 2016; Gamage et al. 2022). In 2020, the agriculture sector demanded globally 11.7 million tons of plastic, which is around 3.3% of the total plastic production (Plastic Europe 2021). Fossil-based polymers dominate today's market. However, the scarcity of petroleum resources and negative environmental impacts, such as soil contamination and plastic residue accumulation, has impulse the search for innovative alternatives. So, the use of biopolymers is also of great interest for the development of alternative more sustainable, eco-friendly, and cost-effective materials for agriculture applications.

Bio-based materials showed a global market capacity of 2.4 million tons in 2021, forecasting an increase to 7.6 million tons by 2026 (European Bioplastics 2021). Biodegradable natural polymers, such as starch, cellulose, chitosan, glucomannan, and sodium alginate, have already been proposed for soil mulching, plant containers, and seed coating owning their natural degradation and soil-enhancing properties (Santos et al. 2020). Agroindustry processing wastes and by-products are usually biopolymer-rich sources and can therefore contribute to a circular economy (George et al. 2020) for mulching purposes.

Plastic mulching films are advantageous from both agronomic and phytosanitary aspects. They can prevent weeds and reduce the need for chemicals, favor the crop by conserving soil moisture and moderating its temperature, and avoid direct contact of produce with dirt and soil. Low-density polyethylene is the most used material, ensuring adequate mechanical resistance, and moisture and optical barrier. However, the mulches must be removed from the field after the crop cycle, demanding hand labor or specific machinery. Plastic residues are often discarded in a dump or burned, resulting in environmental toxic emissions (Immirzi et al. 2009). Biodegradable alternatives can, thus, contour those effects.

Biopolymer mulches can be processed by extrusion, casting, and spraying methods to form films and coatings (Adhikari et al. 2016). The higher costs and poorer mechanical and barrier properties still impose the main challenges for the practical use of bio-based mulches. Ideally, the material needs to stay intact until the end of the crop cycle and then undergo full biodegradation within a few months. Strategies to enhance the material's properties include chemical modification, crosslinking, blending different biopolymers, adding plasticizers, and loading with reinforcement filler. Cellulose fibers, wheat bran, dry algae, and other natural components were added to the polymeric solution to enhance mulch properties (Adhikari et al. 2016).

Biopolymers matrices can also carry active agents such as nutrients, pigments, and growth promoters. Starch and chitosan blend films with the addition of citric acid and black pigments showed potential for application as biodegradable mulching for short-cycle vegetables and flower crops (Brandelero et al. 2019).

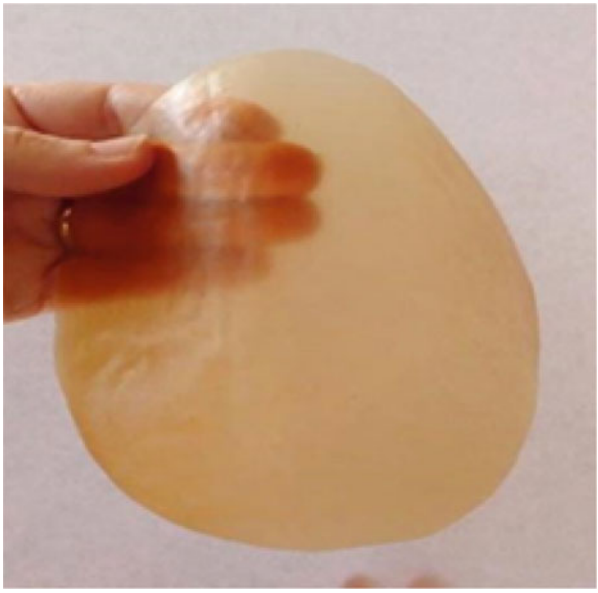

Fig. 7.5 Visual aspect of vinasse-enriched alginate/konjac glucomannan film

As an attempt to propose another alternative use for sugarcane vinasse, films based on alginate and konjac glucomannan enriched with vinasse (as a solvent for biopolymers) were produced by casting and characterized, allowing the recycling of vinasse nutrients into the soil (Fig. 7.5). The films were crosslinked with calcium ions reducing drastically their water solubility and enhancing mechanical resistance (Santos et al. 2020). Compared to control films (without vinasse), vinasse-added ones were more flexible and showed reduced light transmittance at 450 nm.

7.6 Final Remarks

The fate of the large volumes of sugarcane vinasse from ethanol production is a concern. Although fertigation can neutralize the polluting potential of this residue, its adoption is limited to soil characteristics and feasible distances from the producing unities creating exceeding volumes. Finding novel strategies and new opportunities to deal with this problem is a key to achieving sustainability and circular economy goals. Biopolymers and derived materials appear as green and indispensable materials in many applications. These materials should not only fulfill the environmental aspects but also satisfy future requirements for innovative technological solutions. Thus, associating biopolymers to achieve treatment and valorization of this wastewater represents new opportunities. Biopolymers can act as matrices for cell immobilization to remove pollutants and nutrients from vinasse. Emphasis is given to the heterotrophic culture of microalgae to consume organic carbon. Studies

with calcium alginate beads indicate the uptake of carbon, nitrogen, and potassium from vinasse and reuse of the microalgal biomass and metabolites. Other solutions are the development of slow-release fertilizers based on biopolymers and vinasse, and biodegradable mulching films enriched with this wastewater. The entrapment of vinasse nutrients into solid materials can enhance the effectiveness and expand the agricultural use of this wastewater. This multidisciplinary approach expects to inspire future studies concerning alternative biotechnological solutions for agro-industrial by-products.

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Chapter 8
Valorization of Guava Fruit By-Products

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Abstract Guava (*Psidium guajava* L) is grown in many tropical and subtropical countries of the world. Large-scale processing of guava into various products generates a large amount of waste, also called by-products (seeds, peel, pulp residues). They are an abundant and low-cost agricultural waste that is readily available in large quantities. These are mostly discarded, generating a significant environmental impact, and their proper disposal increases costs. The by-products have been extensively characterized, highlighting their fiber content, phenolic compounds with antioxidant activity, as well as lipids. This chapter presents a review of the physicochemical characterization, phenolic compounds identified, and research related to the utilization of these by-products. This identification of compounds allows us to evaluate the multiple possibilities offered by this by-product due to its characteristics and properties.

Keywords Guava · Residue · Bioactive compounds · Dietary fiber · By-products · Antioxidants

8.1 Introduction

Guava (*Psidium guajava* L.) is a tropical perennial fruit of great importance (Nobre et al. 2020). It belongs to the Myrtaceae family. Its cultivation originated in the tropical zone of America, and given its commercial importance it gradually spread to other countries. The main producing countries are India, China, Thailand, Pakistan, Mexico, Indonesia, and Brazil (Nobre et al. 2020; Rajan and Hudedamani 2019). It is characterized as a resistant crop, easy to handle, and high remunerative (Rajan and Hudedamani 2019). In 2019, the world production of this fruit was approximately

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55.85 million tons (Kumar et al. 2022). Guava fruit is consumed fresh and processed. However, most of the production is destined for industrialization (Lira et al. 2009; Mantovani et al. 2004). The food industry processes the fruit into pulp, juices, sweets, and other products (Angulo-López et al. 2021; Nobre et al. 2022; Mantovani et al. 2004). After guava pulping, a large amount of waste or also called by-products is generated (Fan et al. 2022; Kumar et al. 2022; Lima et al. 2022), composed mainly of seeds, peels, and pulp remain (Amaya-Cruz et al. 2015; Angulo-López et al. 2021; Lima et al. 2022; Martínez et al. 2012). These by-products can account for up to 30% of the weight of processed fresh fruit (Fan et al. 2022; Lima et al. 2019; Lira et al. 2009). In Brazil, one of the main producing countries, more than 70 thousand tons of waste are generated per year (Kumar et al. 2022).

In addition to production residues, some fruits are discarded as a consequence of deterioration during marketing, mainly due to the short shelf life of the fruit postharvest (Fan et al. 2022). In Mexico, about 57.70% of the national production is lost during postharvest handling (González-Arias et al. 2021). These by-products are often disposed of in landfills without being treated, causing environmental problems. An important point in the utilization of by-products is the ease of obtaining and the amount of residue produced in one place. The use of guava by-products is feasible from the point of view of access and low cost. As they are generated by the industry, they are easily available in large quantities and at a low cost (Kumar et al. 2022). The use of these by-products contributes to reducing the economic and environmental problems that may be generated by the poor disposal of these wastes (Casarotti et al. 2018).

On the other hand, recent research has awakened interest in fruit by-products. These studies have focused on the physicochemical characterization, identification, quantification, and of bioactive compounds, as well as potential uses in the agroindustry. Some studies have also demonstrated higher nutritional content in by-products compared to the edible portion of the fruit (Can-Cauich et al. 2017; Casarotti et al. 2018).

Therefore, this chapter describes the composition of guava processing by-products. The main bioactive compounds identified in these by-products are presented. Recent studies on the use of bioactive compounds in food and their potential health benefits are also presented.

8.2 Guava By-Products

Guava is recognized for its exceptional nutritional content. It has a higher ascorbic acid content than citrus fruits. It is harvested continuously throughout the year (Lima et al. 2022). This makes it a very profitable and low-cost fruit. Not only the pulp has important bioactive compounds of interest, but it has also been found that in the by-products processing, significant quantities of compounds are present such as fiber, lipids, phenolic compounds, pectins, polysaccharides, and others. An example is the procyanidins, tannins found in the different varieties of guava, but they are

concentrated in the skin and seeds, being to a lesser extent in the pulp (Suwanwong and Boonpangrak 2021). Some of the compounds identified have been associated with the prevention and/or treatment of diseases (Angulo-López et al. 2021; Lima et al. 2022). These guava processing by-products have untapped potential around food science (Kumar et al. 2022).

8.3 Physicochemical Composition

Dietary fibers (DF) are the edible parts of plants, which can be totally or partially fermented in the large intestine and undigested and unabsorbable in the human small intestine (He et al. 2021). According to their solubility in water, they can be classified into soluble (SDF) and insoluble (IDF) FDs. This characteristic is related to fiber components, structure, technological functionality, and physiological effects (Elleuch et al. 2011; He et al. 2022; Lin 2022). Table 8.1 presents the physicochemical composition of guava by-products.

Guava processing by-products have been of great interest as a source of dietary fiber and different antioxidants. The fiber content of guava by-products is higher than in cereals and pseudocereals such as oats, barley, rye, quinoa, amaranth, and chia (Angulo-López et al. 2021).

The high total dietary fiber content of guava by-products, especially the insoluble fraction, is mainly due to the presence of seeds (Amaya-Cruz et al. 2015). The insoluble fraction includes starch, resistant proteins, condensed tannins, lignin, minerals, and insoluble polysaccharides (Amaya-Cruz et al. 2015; Saura-Calixto et al. 2000). To obtain the best gastrointestinal physiological effects of the soluble and insoluble fraction, the IDF/SDF ratio should be between 1.0 and 2.3 (Martínez et al. 2012). As reported by Amaya-Cruz et al. (2015) the ratio for guava by-products is 17.46, much higher than that reported for other fruit residues such as mango and peach at 1.35 and 1.81, respectively. The highest values of IDF/SDF ratio have been

Table 8.1 Physicochemical composition guava by-products

Parameters	Guava by-products
Moisture (%)	3.97(1), 9.3(3)
Proteins (%)	2.07(1), 4.8(3)
Fat (%)	1.20(1), 1.4(3)
Ash (%)	0.83(1), 2.4(3)
Carbohydrates[a] (%)	2.13(1), 22.2(3)
Total dietary fiber (%)	89.80(1), 78.4(2), 69.1(3)
Insoluble fibers (%)	86.10(1), 74.4(2), 57.7(3)
Soluble fibers (%)	3.70(1). 4.3(2), 11.1(3)
Water activity	0.164(1)

(1) Casarotti et al. 2018; (2) Amaya-Cruz et al. 2015; (3) Martínez et al. 2012

[a]Obtained from 100—(moisture + ash + lipids + proteins + total dietary fiber)

reported for cereals. For example, oat bran has a ratio of 5.62 and wheat bran 14.15. Arguably, the insoluble fraction is of greater physiological importance; however, there are still few studies that have quantified this fraction (Amaya-Cruz et al. 2015).

The lipid fraction of guava by-products is mainly composed of unsaturated fatty acids, especially linoleic acid (77.35% of all fatty acids) (Uchôa-thomaz et al. 2014).

8.4 Bioactive Compounds

By-products are a source of bioactive compounds, which due to their antioxidant properties can prevent and fight different diseases, by eliminating free radicals and/or the potential of provitamin A (carotene) (Carvalho Gualberto et al. 2021). Table 8.2 shows the content of bioactive compounds present in guava by-products and the antioxidant activity. The content of antioxidant compounds depends on the fruit variety, being higher in the red-fleshed variety (Lima et al. 2019). This may explain, in part, the differences in the content of phenolic compounds reported. The presence of bioactive compounds such as ascorbic acid, carotenoids, flavonoids, and other phenols is one reason why the utilization of these by-products could offer numerous positive health effects, including the prevention of diseases associated with oxidative stress and cell damage, cardiovascular diseases, as well as decreasing the risk of cancer (Can-Cauich et al. 2017; de Oliveira et al. 2020).

The presence of phenolic compounds in guava by-products indicates that this fraction still contains a significant amount of antioxidant substances (Lima et al. 2019). Table 8.2 can see the content of phenolic compounds of guava by-products, determined by different authors. It varies between 59.25 and 750 mg GAE/100 g. It could be said that this phenolic content is medium-low, according to the classification proposed by (Vasco et al. 2008). The differences in phenolic compound content reported are due to multiple factors, including fruit variety, maturity stage, climate, and especially extraction methods (Vasco et al. 2008).

Guava by-products have a high content of phytochemicals, among which phenolic acids and flavonoids stand out (Lima et al. 2022). The above has made guava by-products a material of study in recent years. Lima et al. (2019) conducted a study where they determined the phytochemical composition, phenolic profile, and antioxidant activity of guava pulp extracts and guava residues. The extraction was performed with ultrasound for 2 min at 25 °C. Ethanol/water solution (30:70,v/v) was used as a solvent. Phenolic profiling was performed by LC-ESI-MS/MS analysis. Among the different guava samples, the residue powder presented the highest content of flavonoids (1006.08 mg QE/100 g), flavonols (352.59 mg QE/100 g), and condensed tannins (1466.9 EC mg/g). The values obtained are higher than those reported by other studies. The authors attribute this to the use of the ultrasound extraction probe, which, unlike conventional extraction methods, ultrasound extraction acts on the walls of the material and contributes to the diffusion of the solvent through the matrix, promoting the release of bioactive substances in a much more efficient way.

Table 8.2 Contents of different bioactive compounds guava by products

Bioactive compounds	Content
Ascorbic acid (mg/100 g)	10.68(4)
Organic acids	
Citric acid (mg/100 g)	16(2)
Malic acid (mg/100 g)	37(2)
Succinic acid (mg/100 g)	9(2)
Tartaric acid (mg/100 g)	178(2)
Total carotenoids (mg/100 g)	0.08(4)
Carotenoids (μg β-carotene/g)	7.91(1); 3(3)
Carotenoids (μg lycopene/g)	4.77(1)
Extractable polyphenols	
Total phenolic (mg GAE/100 g)	253.14(1); 59.25–172.56(2); 750(3); 234.72(4); 432.7(5); 336.30(6)
Total flavonoids (mg CE/100 g)	7.87–44.45(2)[a]; 230(3);114.80(4); 1006.08[a](5); 427.35 (6)[b]
Non-extractable polyphenols	
Hydrolyzable tannins (MGE mg/g)	0.69(3)
Condensed tannins (CE mg/100 g)	1466.9(5); 13.2(3)[c]
Antioxidant activity	
FRAP (μmol TEAC/100 g)	1096.67(4)
ABTS• + (μmol TEAC/100 g)	470(4)
Soluble sugars Monosaccharides and disaccharides (mg/g)	
Fructose	22.68(2)
Glucose	7.02(2)
Oligosaccharide (mg/g)	
Nystose	6.59(2)

(1) Casarotti et al. 2018; (2) Carvalho Gualberto et al. 2021; (3) Amaya-Cruz et al. 2015; (4) de Oliveira et al. 2020; (5) Lima et al. 2019; (6) Kong et al. 2010. Results are expressed on dry basis. *GAE* gallic acid equivalents, *CE* catechin equivalents, *TEAC* trolox equivalent antioxidant, *FRAP* ferric reducing ability of plasma, ABTS• + cation, 2,2- azino-bis (3-ethylbenzothiazoline)-6-sulfonic acid

[a] mg QE/100 g: mg quercetin equivalent for 100 g of sample

[b] mg rutin equivalent (RE)/100 g

[c] PA mg/g: proanthocyanidins/g

The main polyphenols of the guava by-product are ellagic acid (Lima et al. 2019), *p*-hydroxybenzoic acid (4-hydroxybenzoic acid), and epicatechin (Amaya-Cruz et al. 2015) (Fig. 8.1).

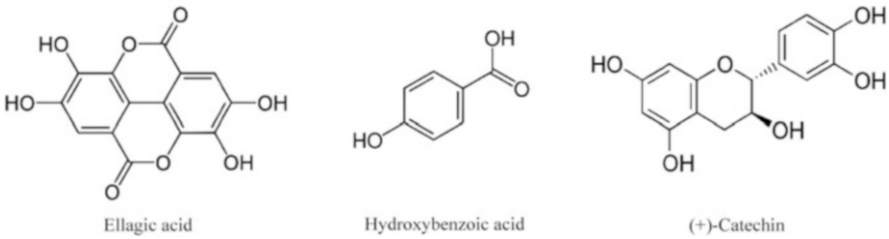

Fig. 8.1 Chemical structure of the main polyphenols of guava by-product (Amaya-Cruz et al. 2015; Lima et al. 2022)

8.4.1 Flavonoids

Differences between flavonoid contents reported in different studies are related to the extraction method, measurement technique, by-product status, etc. (Pierson et al. 2014; Suwanwong and Boonpangrak 2021). Flavonoids have been identified in guava by-products such as seeds, peel, and pulp remain. These by-products have a high concentration of flavonoids and flavonols compared to fruits (Lima et al. 2022). Flavonoid content is generally expressed as milligram catechin equivalents for 100 g of sample (mg CE/100 g), milligram quercetin equivalent for 100 g of sample (mg QE/100 g), or milligram rutin equivalent for 100 g of sample (mg RE/100 g). Kong et al. (2010) reported content of 427.35 mg RE/100 g, in industrial residues of pink guava, after optimizing the extraction process.

8.4.2 Condensed Tannins

According to research conducted by Lima et al. (2019), the condensed tannin content in the by-products is higher than in the fruit, with values of 1466.9 EC mg/100 g and 1081 EC mg/100 g, respectively (see Table 8.2). Procyanidins have been found in different guava varieties; these are found in higher concentrations in the skin and seeds (Suwanwong and Boonpangrak 2021).

8.5 Bioactive Compounds Identified in Guava By-Products

The main compounds identified in guava by-products are phenolic acids and flavonoids. The polyphenolic profile is presented in Table 8.3. The main compounds identified include ellagic acid, vanillic acid, gallic acid, quercetin, phenolic acid, 4-hydroxymethylzenzoic acid, umbelliferone, mandelic acid, syringaldehyde, galangin, eriodictyol, hispidulin, taxifolin, carnosol, methoxyphenylacetic acid, salicylic acid, fustin, and coniferaldehyde (Amaya-Cruz et al. 2015; Lima et al. 2019).

Table 8.3 Identification of phytochemical compounds of guava by-products by HPLC-DAD-MSD

Bioactive compounds	Content
Polyphenolic profile	
Phenolic acids	
Cinnamic acid (mg/g)	0.179(2)
Salicylic acid (mg/g)	0.0108(2)
Chlorogenic acid (ng/g)	1.9(1); 0.0124(2)[a]
Gallic acid (mg/g)	LDL(1); 0.3504(2)
p-Coumaric acid (ng/g)	0.5(1); 0.150(2)[a]
Caffeic acid (ng/g)	0.5(1)
Sinapic acid (ng/g)	0.6(1); 0.0406(2)[a]
Ellagic acid (ng/g)	0.6(1); 1.600(2)[a]
p-Hydroxybenzoic acid (ng/g)	3.2(1)
Protocatechuic acid (mg/g)	LDL(1); 0.0924(2)
Methoxyphenylacetic acid (mg/g)	0.1021(2)
Vanillic acid (mg/g)	1.2346(2)
Syringic acid (mg/g)	0.032
Rosmarinic acid (mg/g)	0.0074
Ferulic acid (ng/g)	0.8(1); 0.0254(2)[a]
Flavonoids: Flavanols	
Epigallocatechin gallate	0.6(1)
Epicatechin (mg/g)	3.7(1)
Quercetin 3-O-rutinoside	0.6(1)
Quercetin (mg/g)	0.1(1); 0.2363(2)
Kaempferol (mg/g)	2(1)
Catechin (mg/g)	0.3(1); 0.0283(2)
Gallocatechin gallate	0.2(1)
Apigenin (mg/g)	0.0053(2)
Galangin (mg/g)	0.0224(2)
Naringenin (mg/g)	0.0164(2)
Aromadendrin (mg/g)	0.0035(2)
Taxifolin (mg/g)	0.0482(2)
Myricetin (mg/g)	0.1575(2)
Flavonones	
Eriocitrin	0.3(1)
Naringin	0.5(1)
Hydroxybenzaldehydes	
Vanillin (mg/g)	LDL(1); 0.0441(2)

(1) Amaya-Cruz et al. 2015; (2) Lima et al. 2019. Results are expressed on dry basis. *LDL* lower than detection time
[a]mg/g

Guava residues are a potential source of bioactive compounds. These could be exploited in the food, pharmaceutical, and cosmetic industries (Carvalho Gualberto et al. 2021).

8.6 Utilization of Guava By-Products

8.6.1 Antioxidant Dietary Fiber

Antioxidant dietary fiber is a term used to refer to materials with high fiber content and associated phenolic compounds. Guava processing by-products could be a good source of antioxidant dietary fiber, due to the high content of fiber and associated phenolic compounds (Jiménez-Escrig et al. 2001). These phenolic compounds have been identified mainly in the insoluble fraction of the fiber (Quirós-Sauceda et al. 2014). This fraction exceeds 50% in guava by-products. Antioxidant dietary fiber possesses techno-functional properties, important at the industrial level. Several studies have evaluated the influence of the incorporation of these fibers in functional food formulations. Among the physicochemical properties presented by the fiber are water holding capacity (WHC) (2.01–25.03 g/g), oil holding capacity (OHC) (0.65–29.00 g/g), swelling capacity (WSC) (0.95–23.90 mL/g), glucose adsorption capacity (GAC) (0.17–4.65 mmol/g), cholesterol adsorption capacity (CAC) (0.03–37.10 mg/g), and viscosity, among others. These techno-functional properties of the fiber are responsible for different physiological functions such as reducing the risk of obesity, diabetes, cancer, and intestinal diseases. In addition, high dietary fiber content is indicative of the prebiotic potential of by-products.

Antioxidant dietary fiber can be fermented by bacterial microflora, and its metabolites have been reported to exert greater beneficial effects than its precursors (Pérez-Jiménez et al. 2013; Saura-Calixto 2011). The mechanism of action of polyphenols will depend on their nature. Extractable polyphenols can be absorbed in the small intestine. Non-extractable polyphenols reach the colon bound to other non-digestible compounds such as dietary fiber, starch, proteins, and other non-digestible compounds. In the colon, the dietary fiber is fermented by the action of the bacterial microflora, and as a consequence, some phenolic compounds are released. These non-digestible compounds, such as hydrolyzable tannins, could exert an important beneficial effect on the colon, promoting intestinal health through increased antioxidant and antiproliferative capacities (Amaya-Cruz et al. 2015; Pérez-Jiménez et al. 2013). Some compounds released in the colon as a consequence of fiber fermentation have been related to the prevention and treatment of cardiovascular diseases and obesity (Amaya-Cruz et al. 2015; Pérez-Jiménez et al. 2013).

The incorporation of guava by-products may have positive effects on the physicochemical properties of foods; however, the possible beneficial effects on health associated with fiber consumption (soluble and insoluble) should be tested in physiological studies (Grigelmo-Miguel and Martín-Belloso 1999).

8.6.2 *Beneficial Health Effects Related to the Consumption of Guava By-Products*

Recent in vitro and in vivo research has demonstrated the beneficial health effects associated with the consumption of guava and its by-products. These effects are mainly due to the high contents of biologically active phytochemicals, phenols, vitamins, and dietary fibers (Lima et al. 2022). The intake of phenols present in guava by-products could benefit the composition of the gut microbiota and protect probiotic bacteria from the harsh conditions encountered during the gastrointestinal passage, as well as in different foods, which could explain the wide range of health-promoting effects induced by these components (de Oliveira et al. 2020; de Souza et al. 2019).

Dietary fiber intake from guava by-products could increase fecal volume and mass, mainly due to its high content of the insoluble fraction (Martínez et al. 2012). It could also be reflected in a decrease in body weight gain of 8% (Amaya-Cruz et al. 2015).

Amaya-Cruz et al. (2015) evaluated the in vitro activity of α-amylase in the presence of powdered by-products of different fruits, including guava by-products. These determined a higher reduction of enzyme activity, in the by-product powder samples. According to the analysis presented by the author, this higher inhibition activity is related to the content of free polyphenols in the extracts, because phenolic compounds interact through their hydroxyl groups with the enzyme binding site, which causes a change in the molecular configuration and as a consequence decreased enzymatic activity (Amaya-Cruz et al. 2015; lo Piparo et al. 2008). Reduced α-amylase enzymatic activity can reduce the rate of glucose absorption and thus postprandial glucose levels (Amaya-Cruz et al. 2015).

Other benefits associated with dietary fiber consumption include antioxidant, anti-cancer, anti-diabetic, anti-obesity, and other related effects. However, despite the current evidence, more clinical studies are needed to evaluate the effects on human health (Lima et al. 2022).

8.6.3 *Incorporation in Food*

The use of by-products by incorporating them into food formulations responds to several objectives: improving the techno-functional properties of foods, improving the nutritional profile, and providing functional properties through the bioactive compounds present in the by-products. Studies have shown that it can be successfully incorporated into a variety of food products (Casarotti et al. 2018). Because of the physicochemical characteristics of guava by-products, the addition in fermented food formulations presents an advantage since they can act as protectors of probiotics against adverse conditions through the human gastrointestinal tract. The

fiber content may also present a prebiotic potential, acting in synergy with probiotics in the gut after ingestion (Lin 2022).

The addition of guava powder (5%) in a bread formulation increased crude fiber content (0.92–2.45%) and total phenolic content (14.46–103.77 mg GAE/100 g), in addition to improving aspects such as hardness, increasing volume, and overall acceptability compared to the control, without affecting protein content and calorific value (Lin 2022).

8.6.4 Obtaining Pectin

Pectin is related to cholesterol reduction. This polysaccharide is of great importance in the industry. Because of its properties, it is used in the stabilization of emulsions and its ability to form gels. It is present in guava by-products. The extraction process involves a series of operations such as blanching, extraction (nitric acid solvent), filtration, and separation. The optimum conditions, time, temperature, and pH for pectin extraction were 45 min, 80° C, and 5.0 respectively, with a yield of 0.06% in powder form (Sharma and Kaur 2017).

8.6.5 Energy Production

The use of by-products as feedstock in renewable energy generation has been of great interest because it does not compete with the food supply and reduces environmental impact (González-Arias et al. 2021). According to González-Arias et al. (2021), guava residue is a suitable feedstock for gasification under supercritical water conditions. They evaluated for the first time the gasification of guava residue, with the objective of studying the reaction parameters of the gaseous products and the impact of temperatures in relation to the feed. Using a batch reactor, they reported temperatures between 673.15 and 773.15 K with biomass/water ratios of 1:1, 1:4, and 1:6. After the characterization of the products obtained in the different phases (solid, liquid, and gas), they concluded that as a preliminary stage the high-temperature operation and biomass/water mass ratio improved the gas yields (mol/kg) of about 4.137 for CH_4, 6.705 for CO_2, and 7.743 for H_2, while the gas selectivity and efficiency for hydrogen were 65.26% and 58.94%, respectively.

8.7 Conclusions

Guava processing by-products are materials with numerous bioactive compounds, including phenols, carotenoids, dietary fiber, antioxidants, vitamins, lipids, and pectins, among others. From the detailed composition of these compounds, possible

uses can be generated, and a more adequate utilization can be made. The extraction of valuable compounds such as proteins, fibers, phenols, or sugars and their incorporation as raw material in the industry contributes to the current search for low-cost and more environmentally friendly sources of active compounds.

There are several studies where different alternative uses of guava by-products have been presented; however, it is still necessary to identify the mechanisms by which they confer health benefits, and bioavailability studies of the active components of guava residues are scarce.

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Chapter 9
Valorization of Coffee By-Products: An Overview

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Abstract The world consumers and companies are facing a shortage of resources of different nature, as well as dealing with a recent pandemic and growing chronic diseases associated with different food products that in their preparation are enriched or added by substances or compounds derived from chemical synthesis; for this reason, the search for food products with biologically active and environmentally friendly properties is increasing in the markets from all over the world. These compounds are derived from plant, animal, and mineral products, especially from agro-industrial by-products that arouse the interest of the scientific community as an available, profitable, and sustainable source of a wide range of biologically active compounds. For this reason, the objective of this review focuses on one of the agricultural sectors with the highest production in the world such as the by-products derived from coffee processing, focusing on the biological potential, and the profile of bioactive compounds, of recent work, carried out by various researchers around the world. This review evaluates previous work done by different researchers on the potential represented by coffee by-products as a source of bioactive compounds such as fiber, carbohydrates, polyphenols, flavonoids, anthocyanins, procyanidins, tannins, caffeine, chlorogenic acid, and other organic compounds. These identified compounds are of vital importance to be studied separately so that each molecule has properties according to its biological activity, in addition to some food products that have already been fortified or enriched with compounds derived from the coffee pulp as well as the production of functional drink, honey, tea, syrup, and flours,

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making clear the high nutritional and nutraceutical value of agro-industrial by-products.

Keywords Agro-industrial residue · Bioactive compounds · Coffee pulp · Polyphenols · Flavonoids

9.1 Introduction

At present, the world faces an eminent concern about the scarcity of different products of nature derived from domestication or agro-industrial crops, as well as different evils that affect the societies of the world, such as the recent pandemic and many other chronic diseases associated with eating habits. The agro-industrial sector worldwide, according to the generation of waste, is worrying the abysmal amount that occurs in the agricultural sector due to the problem of its disposal, generating different environmental problems (water, air, and soil), as well as a challenge for the agro-industrial sector that seeks to take advantage of and optimize through different biotechnological strategies the production and extraction of molecules of the high added value of such waste, becoming an important source of natural resources, in obtaining biologically active compounds. Recent studies by various researchers who focus their attention on coffee pulp have been able to verify the presence of these components, which stand out in greater proportion phenolic compounds, organic acids, carotenoids, and flavonoids among others (Shirahigue and Ceccato-Antonini 2020), with attributions of multiple biological properties such as anticancer, antioxidant, antimicrobial, probiotic, prebiotic, and immune system modulators (Leyva-López et al. 2020).

The main wastes generated in agribusiness during the post-harvest and processing of raw materials are leaves, stems, roots, bark, pulp, straw, bagasse, seeds, tubers, fruits, vegetables, and shavings among many others (Del Rio Osorio et al. 2021), which have represented an environmental problem for the sector, due to the large quantities produced, and there is still no action plan in underdeveloped countries for the processing of waste, where ecosystems such as aquifers, flora, and fauna are affected, in this sense of being an organic matter with capacities already mentioned, comprising active substances or that can trigger a physiological response in the living being (Leyva-López et al. 2020). The production of primary and secondary metabolites for pharmacological, food, cosmetic, and textile purposes has been sought (Raven et al. 2019) naturally in contrast to synthetic ones. The production of secondary metabolites derived from plants such as flavonoids, thiosulfinates, glucosinolates, organic acids, and saponins that have properties like antimicrobial, antioxidant, and anticancer agents. One of the most important groups is phenolic compounds, which include terpenes, aliphatic alcohols, aldehydes, ketones, acids, anthocyanins, and isoflavonoids (Shirahigue and Ceccato-Antonini 2020). The present review is focused on describing the potential of the natural resource coffee pulp, which represents one of the primary wastes of coffee cherry processing where a large amount of pulp is obtained, which would be around 1 ton for every 2 tons of

cherry coffee; said coffee pulp is essentially rich in carbohydrates, proteins, and minerals (especially potassium) and also contains appreciable amounts of tannins, polyphenols, and caffeine (Manasa et al. 2021). It is chemically composed of a large number of useful substances to be used in different industries, and it becomes necessary to perfect biotechnological developments for the use of renewable energies to mitigate climate change. In this sense, biomass obtained from organic matter has become the main advantage and a more popular alternative than other renewable energy sources, such as solar and wind energy (Ramos-Hernández et al. 2021).

9.2 Coffee Description

With the word coffee, we designate one of the most popular drinks (Siedentopp 2009), treasured by millions of people around the world, resulting from the roasted seeds of trees belonging to the Rubiaceae botanical family. The coffee plant is extremely sensitive, and it only grows in the tropics (Fig. 9.1), which for its development needs heat and humidity at constant temperatures between 17 °C and 23 °C (Miele 2006). The optimal height for its cultivation is between 600 and 1200 m above sea level. This species is believed to have its origins in Africa and eventually spread to countries around the world (Ferreira et al. 2019). The production of the coffee plant from the highlands, known as "high grown," is especially appreciated by connoisseurs due to its excellent quality (Miele 2006). But only two

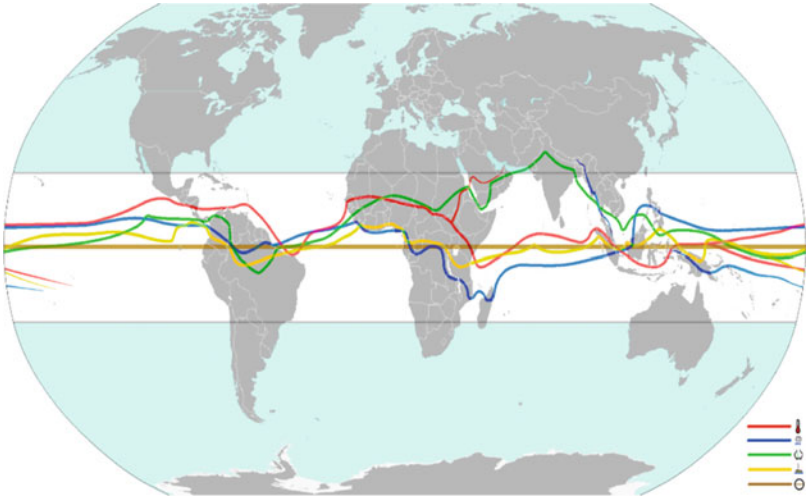

Fig. 9.1 The map of the tropical region is crossed by climatic equators that distinguish them, such as the thermal equator (in red), the tropical rain belt (in blue), the equatorial trough (in green), and the equatorial calm zone (in yellow). (Adapted from https://hmong.es/es/Climas_tropicales)

plant species are economically relevant as a source of coffee: Arabica (*Coffea arabica*) and Robusta (*Coffea canephora*) (Petruzzello 2021).

Coffee is one of the most complex natural products, due to its history, its trade, and its chemical richness, made up of organic acids, aldehydes, ketones, esters, hydrocarbons of low molecular weight, amino acids, caffeine, carbohydrates, proteins, trigonelline, lipids, glycosides, and minerals; each of them contributes with flavor (more than 400 hundred organic and inorganic compounds) and characteristic aroma (more than 6 hundred compounds) mostly in trace concentrations (Parada 2017).

9.3 Coffee Botany

Botanists consider coffee trees to be all tropical plants of the *Rubiaceae* family, which produce seeds that resemble coffee beans. Several hundred species have been described under the family *Rubiaceae*, but the classification of the genus *Coffea* remained complex and confusing (Clifford and Willson 1985). The family consists of about 500 genera and more than 6000 species, mostly tropical trees, and shrubs (Table 9.1). Within the genus *Coffea*, there are more than 100 species, all of them native to Africa (Rojo and Pérez-Urria Carril 2014).

Figure 9.2 shows the structure of a coffee cherry, under the leathery epicarp (skin), which is green at first and turns red with increasing maturity, is the sweet and soft mesocarp (pulp). Underneath is the strongly developed endocarp (parchment), which encloses the two seeds (endosperm) called coffee beans, which are covered by their silvery skin, a thin integument (Klingel et al. 2020).

9.3.1 Coffea arabica

Coffea arabica was first described in 1753 by Linnaeus. It is a large shrub, about 5 m high, with oval leaves and bright dark green. Flowering occurs after the rainy season, and its flowers are white, sweet in aroma, and arranged in clusters. The fruits, green and oval, turn red when ripe, after 7–9 months. Each fruit usually contains two flat, flat-like seeds (the coffee beans). *Coffea arabica* is grown throughout Latin America, central and east Africa, India, and Indonesia. Its best known varieties are

Table 9.1 Botanical classification (ICO n.d.)

Family	Gender	Species (among many others)	Varieties (some examples)
Rubiaceae	*Coffea*	*arabica*	*Typical*
		canephora	*Robust*
		liberica	

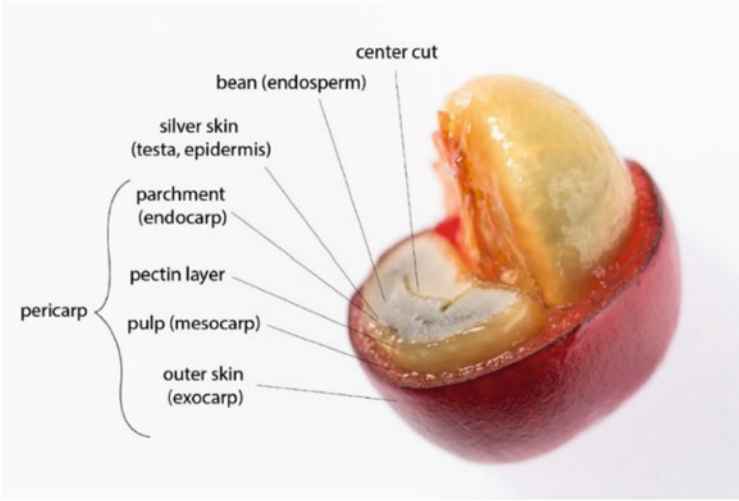

Fig. 9.2 Cross section of a coffee cherry with its different layers (Klingel et al. 2020)

"*arabica*" *(typica)* and "*bourbon*," but from these new strains and different cultivars have been developed, such as "*Caturra*," "*Mundo Novo*," "*Tico*," "*San Ramón*," "*Moca*," "*Maragogipe*," "*Columnaris*," or "*Blue Mountain*" (Bento et al. 2022; dos Santos et al. 2020; Rojo and Pérez-Urria Carril 2014).

Due to heterogenous populations within the cultivated groups, it is difficult to differentiate "cultivars" in the same subpopulation. Therefore, the term variety (or cultivar) should be used only for long-term cultivated lines (Banerjee 1992).

9.3.2 Coffea canephora

It is a robust tree with a shallow root that can reach 10 m in height. The fruit is rounded and takes up to 11 months to ripen. Its seed is elongated and smaller than that of *C. arabica*, while the leaves are usually larger. The robust coffee is grown in Central and West Africa, throughout Southeast Asia, and somewhat in Brazil, where it is known as "*Conillón*" (Rojo and Pérez-Urria Carril 2014).

9.4 Coffee Production in the World

Coffee is one of the main agricultural primary export products worldwide, and one of the main sources of economic income for producing countries, occupying second place in international trade only behind oil (Villalta-Villalobos and Gatica-Arias 2019). The production of coffee according to the varieties occurs between the

semi-warm tropics and fresh tropics. The natural habitat of all coffee species is the understory of African tropical forests. Many forms of *C. canephora* can be found in equatorial forests from Guinea to Uganda, considering that natural populations of *C. arabica* are restricted to the highland forests of southwestern Ethiopia. They require for their development altitudes of 400–2800 m above sea level while *C. arabica* grows best in a subtropical climate, free of frost and without strong winds; the most frequent altitudes range from 600 to 2000 m in the tropics, although in high latitudes it is cultivated below 600 m; *robusta*, *liberica*, and *excelsa* coffees are more tolerant to heat and thrive in the tropics from sea level to 1100 m. The altitude of the coffee plantations is strongly linked to the quality of this; the best qualities are between 900 and 1200 m, while the temperature range starts at 5–30 °C, with optimal averages for production between 16 °C and 22 °C, an optimal night and day of 17 °C and 23 °C, respectively. The damage begins when it passes the limits of 13 °C and 27 °C. Average temperatures below 16 °C and above 23 °C are not suitable, with the optimum being 18–21 °C. Above 24 °C, net photosynthesis begins to decline and nullifies at 34 °C.

The optimal range is 15.6–21.1 °C for *C. arabica* and 18.3–26.7 °C for *C. robusta*; these plants grow better in relatively humid and cold environments, but without frost or cold fronts. In matters of precipitation, the optimal annual rainfall accumulated is 1200–1800 mm for *C. arabica* and 1900–2500 mm for *C. robusta*; in some places, rainfall is supplemented by irrigation. A good seasonal distribution of rain should be short dry periods distributed over 9 rainy months, followed by 3 dry months with approximately 25–50 mm of rain to induce next season flowering (Ariel et al. 2020).

In Mexico, coffee farming is considered a fundamental strategic activity, because it allows the integration of productive chains, the generation of foreign exchange and jobs, the way of subsistence of many small producers and around 30 indigenous groups, and recently, enormous ecological relevance, since it provides environmental services to society since 90% of the area cultivated with coffee is under diversified shade that contributes to preserving biodiversity. However, the relevance of the coffee sector has been immersed in recurrent crises due to the fall in prices in the international market (Center for Studies for Sustainable Rural Development and Food Sovereignty, CEDRSSA 2018).

9.4.1 Coffee Market

Coffee is grown near equatorial regions worldwide in developing countries such as Brazil, Vietnam, and Colombia as the top three producers (Bhandarkar et al. 2021) and consumed by developed countries. It is a cash crop costing around 141 US cents per pound in June 2021. Total coffee exports worldwide accounted for 7.7 million tons from June 2020 to May 2021, with an estimated production of over 10 million tons. The soil conditions prevailing in the globe's intertropical and equatorial belt

determine the design of the commercial chain for coffee transactions worldwide (Vegro and de Almeida 2019).

9.5 Processing of Coffee Pulp

Processing should begin on the same day of harvest to avoid undesirable fermentations and reduce the risk of mold contamination, starting with the fruit pulp, rich in nutrients and moisture. This is a critical point in the preparation of coffee and can often jeopardize a whole year of work in the care of the plants. Whenever possible, cherries must pass through washing machines and separators. In this process, the rocks and impurities are removed, and the cherries are separated by density: on the one hand, the lightest cherries (floaters—the dried and overripe cherries) and on the other hand the heaviest (the immature and ripe cherries), which allows the separation of cherries with different levels of humidity, facilitating drying and homogenizing the batch of coffee (Illy and Viani 2004). During the processing of coffee beans many by-products are generated, such as skin, pulp, mucilage, parchment, silver skin, and immature/defective coffee beans; about 50% of the coffee fruit is discarded and can contaminate the environment.

9.6 Bioactive Compounds

Bioactive compounds are essential or non-essential compounds found in nature or created during the processing of food or medicinal plants and can modulate different biological activities, benefiting health (Martín Ortega and Segura Campos 2018), with the ability to interact with one or more components in living tissues and exert a wide range of effects; today the interest to incorporate functional and natural food additives has gained significant momentum because consumers are increasingly aware of the benefits of promoting good health. Interest in bioactive compounds for application in foods in different ways continues to grow, driven by ongoing research efforts to identify the properties and potential applications of these substances, primarily extracted from natural sources (Leyva-López et al. 2020).

The coffee pulp contains carbohydrates, proteins, fibers, fats, and antioxidants such as phenolic compounds, chlorogenic acid, epicatechin, and caffeine (Sangta et al. 2021). The main challenge currently is to use the inedible parts of natural matrices, such as waste or by-products, which still contain a large number of different bioactive compounds with significant human health benefits for use in the food industry (Vilas-Boas et al. 2021). Some of the most important bioactive compounds will be described in the following sections.

9.6.1 Polyphenols

They are natural compounds synthesized exclusively by plants, with chemical characteristics related to antioxidant phenolic substances. These molecules or classes of substances are mainly present in fruits, vegetables, green tea, and whole grains, participate in the defense against ultraviolet radiation, and are abundant secondary metabolites with a wide range of biological activities; in food, polyphenols can contribute to bitterness, astringency, color, taste, odor, and oxidative stability (Pandey and Rizvi 2009). Polyphenols possess a broad spectrum of biological activities such as α-glucosidase inhibitory, antihypertensive, and antioxidant activities. Polyphenols are aromatic compounds that carry one or more hydroxyl groups, which are divided into phenolic acids and flavonoids. Phenolic acids are further classified as hydroxybenzoic acids (e.g., gallic acid and related derivatives) and hydroxycinnamic acids (e.g., caffeic acid and related derivatives) (Martínez-Alemán et al. 2019). Flavonoid subtypes include flavonols, flavones, isoflavones, flavanes, catechins (flavan-3-ols), anthocyanins, and chalcones (Ageorges et al. 2014). Phenolic compounds from coffee by-products can be obtained by different extraction techniques, including conventional (solid-liquid and liquid-liquid) and unconventional (ultrasound, microwave, supercritical fluid, subcritical water, pulsed electric field, and fermentation) methods. The main phenolic compounds reported in coffee by-products are chlorogenic acid and its derivatives (Bondam et al. 2022).

9.6.2 Flavonoids

The polyphenols are a large group in the secondary metabolites constituting chemically complex and diverse compounds and are found in the form of glycones or glycosides in many fruits and vegetables. These compounds can be classified into flavones, flavonols, flavanols, flavanones, isoflavones, and anthocyanins. Flavonoids are abundant in plants and are well studied due to several beneficial human health supporting effects such as protecting the cardiovascular system in addition to having antidiabetic, anti-obesity, and anticancer effects (Ballard and Maróstica 2019), by providing positive effects on the maintenance of health and the prevention of diseases. Flavonoids are also used as nutraceuticals because of their biological activities including antioxidants, anti-inflammatories, antiallergic, antimutagenic, cardioprotective, modulators of enzymatic activity, and anticancer activity, among others. The flavonoids present in the coffee pulp contribute to almost two-thirds of the phenolic compounds; most of them are glycosides, some are esters, and are rarely free compounds. The radical uptake capacity of flavonoids is directly affected by glycosylation. Glycosides are less active than aglycone (Myo et al. 2021).

9.6.3 Tannins

Tannins are a water-soluble group of polyphenols, with molecular weight from 500 to 20,000 Da, widely distributed in plants and fruits, produced during stress; exert a protective role, including photoprotection against UV radiations and free radicals and defense against other organisms and environmental conditions, such as drought; and show antioxidant activity (Fraga-Corral et al. 2021). Tannins can be divided into two types, condensed tannin found in the skin and wood of the tree, e.g., in cinnamon and cinchona peel. The second is hydrolyzable tannin that is common in leaf pod and breaks off the tree, having two parts: glucose or polyols and phenolic acids such as gallic acid, hexahydroxydiphenic acid (HHDP), or its derivatives. It bounds to the protein to become a more complex one that barely degrades in the acid-alkaline state (Rakitikul 2017). Together, coffee by-products have significant potential to be used as additives in food products. In dermatology, the antioxidant properties of coffee by-products could protect the skin against damage induced by ultraviolet radiation. In addition, the polyphenol content could be used for patients with alopecia, acne vulgaris, fungal infection, hyperpigmentation, or skin aging (Lestari et al. 2022).

9.6.4 Procyanidins

Procyanidins are widely distributed in the leaves, fruits, bark, and, less commonly, in the wood of a wide spectrum of plants. About 50 procyanidins, from dimers to pentamers, have been isolated and their structures have been defined. The 2 R, 3 R - (2,3- cis)-procyanidins linked by interflavonoid bonds (4β → 8)- and/or (4β → 6) occur more frequently. Many plants contain mixtures of procyanidins 2R, 3R- (2,3—cis) and 2R, 3S- (2,3- trans), but compounds of stereochemistry anterior R usually predominate. Procyanidins have been reported in various studies where research has shown to have biological activities such as antioxidants, anticancer, antiatherosclerosis, hypoglycemic, hypotensive, and hypolipidemic. The physiological functions of procyanidins vary according to their structure, such as the position of the interflavonoid bond and its degree of polymerization (Yang et al. 2021). Procyanidins are produced by oxidative condensation of units of (+)-catechin and/or (−)-epicatechin, e.g., procyanidin dimer in grape seeds. Procyanidins have antioxidant activity and the ability to specifically bind to proteins and regulate cell signaling pathways. Therefore, they have potential preventive use in cancer, inflammation, cardiovascular diseases, diabetes, and autoimmune diseases (Šelo et al. 2022).

9.7 Use of Coffee Waste

In recent years, biotechnological processes offer great opportunities in the use and valuation of agro-industrial waste products, taking advantage in this sense of the entire coffee plant such as coffee pulp, husk, leaves, stem, bark, and roots, which represent an economic value and rich in organic nature, which makes it an ideal substrate for the production of value-added products such as microbial agents, compost, fertilizer, and livestock feed (Pandey et al. 2000), as well as numerous studies that have been developed for the conversion of coffee by-products such as ethanol, enzymes, organic acids, flavor and aroma compound, edible fungi, gallic acid, lactic acid, solutions and alternatives for the elimination of coffee residues, polyphenols, polyhydroxyalkanoates, and lipids (Table 9.2, Hikichi et al. 2017).

9.8 Conclusions

Nowadays it is important to recover the various types of agro-industrial waste, due to its low cost of operation and acquisition of same, which is available in enormous quantities, and that its use is an important source of added value for production through bioprocesses in obtaining products such as secondary metabolites, enzymes,

Table 9.2 Coffee-derived subproducts according to various researchers

Product	Part of the plant used	Authors
Biodiesel	Waste from coffee wells, coffee husk	Thoppil and Zein (2021) and Emma et al. (2022)
Caffeine and phenolic compounds	Coffee parchment	Mirón-Mérida et al. (2019) and Bondam et al. (2022)
Carotenoid	Coffee waste	Moreira et al. (2018)
Prebiotic drink	Coffee pulp	Patil et al. (2022)
Ethanol	Coffee mucilage	Orrego et al. (2018)
Protein fraction: nitrogen and amino acid profiles	Silver leather	Machado et al. (2020)
Potential source of fiber for bread making	Coffee pulp	Rosas-Sánchez et al. (2021)
Isoflavones and lignin	Green coffee	Angeloni et al. (2020)
Coffee liqueur	Coffee grounds	Masino et al. (2022)
Melanoidins and biosugars	Coffee flower	Nguyen et al. (2019)
Pectins and polyphenols	Coffee pulp	Manasa et al. (2021)
Packaging films	Green coffee	Vidal et al. (2022)
Procyanidins	Coffee pulp	Wong-Paz et al. (2021)
Substrate for fungi	Coffee pulp	Chai et al. (2021)
Trigonelline and caffeine	Arabica and Conillón coffee flowers	de Abreu et al. (2021)

organic acids, functional foods, animal feed, pigments, aromatic compounds, biofuels, biosurfactants, and biofertilizers, among many others. Therefore, it is worth mentioning that the use of this waste may impact in the coming years the reduction of the problem that they represent as pollutants to the environment, in addition to the fact that bioprocesses are allowed to scale and continue with the development of new technologies to improve the quality of life of the human being.

9.9 Final Comments

This review shows to the lecturer the complex theme of scientific, technological, social, and economic research derived from the use of agro-industrial waste, highlighting the contents that coffee by-products present, presenting some of the most recent research work published, and also shows the variety of products that can be used to benefit food processing, pharmaceutical, textile, and cosmetic sectors.

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Chapter 10
Valorization of Tomato Fruit Processing Residues

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Abstract Plant-based foods are products highly rich in biologically active compounds that bring important benefits to consumer health. Tomato is a berry of higher production worldwide. Its versatile flavor allows its consumption in different presentations, from fresh fruit to a diverse variety of products such as pasta, juices, purees, sauces, and canned tomatoes, among others. The processing of the tomato fruit generates important residues that include skin, seeds, a fraction of the pulp, as well as other residues. These vegetable residues contain bioactive compounds such as sugars, fiber, protein, vitamins, minerals, as well as pigments and oleoresins with possible beneficial applications in some industrial areas (food, pharmaceutical, among others). The revaluation of waste generated in the processing of tomato fruit includes the application and refinement of a series of technologies that allow recovering and extracting compounds of interest. This chapter discusses the nutritional value of tomato residues as well as technologies for their extraction and possible applications.

Keywords Tomato residues · Tomato by-products · Tomato by-products valorization · Extraction technologies · Bioactive compounds · Carotenoids

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10.1 Introduction

Tomato is one of the most important vegetables worldwide. It is a vegetable rich not only in flavor, but in nutritional value to be a source of multiple vitamins, minerals, proteins, essential amino acids, monounsaturated fatty acids, and other compounds of biological value as the case of carotenoids and phytosterols (Ali et al. 2021). Tomato fruit production has increased significantly over the last few years. The latest figures reported by the FAO estimate a world production of 180 million tons in 2018 alone (Food and Agriculture Organization of the United Nations 2020b). The tomato is not only produced for fresh consumption, but about 40 million tons produced in the world annually are destined for the food processing industry to produce commercial by-products, which include canned tomatoes, sauces, pasta, tomato soup, tomato puree, dried tomatoes, or dehydrated pulp (Liadakis et al. 2022). Despite the notable consumption of fresh tomato and tomato by-products, there is a large amount of loss and waste of both fresh tomato and waste produced by the industry commonly called tomato pomace that includes peels, seeds, and some residual tomato tissue. The strategies implemented to revalue fresh tomato waste and tomato by-products, and with it, formulate fertilizers, livestock feed, compost, or disposed are not enough to take advantage of the large amounts of tomato waste that generate a large environmental impact in terms of agriculture and environmental footprint of food (Szabo et al. 2022; Urbano et al. 2022).

The analysis of tomato residues has shown that they have important bioactive compounds that can be extracted and recovered through the applications of various technologies characterized by being more eco-friendly, fast, safe, and simple compared to traditional technologies. The recovery of such compounds has great applications in various industrial areas, mainly the pharmaceutical and food industry for the formulation of supplements and compounds of added value to foods that offer greater benefits to the health of the consumer.

10.1.1 Tomato Fruit

Tomato is a fruit native to South America, domesticated in Mexico, and grouped within the vegetables. This fruit is an important source of vitamins, carotenoids, minerals, soluble sugars, fiber, organic acids, and proteins, has a low caloric value of 17 kcal/100 g, and is characterized by a high content of water (90–94%) (Fernández-Ruiz et al. 2004).

The nutritional value of the consumed tomato is not very high in the USA. However, high level of consumption in many countries makes this crop one of the main sources of vitamins and minerals (Blancard 2011).

The popularity of tomatoes for commercial or domestic purposes has gradually increased to become one of the most cultivated fruits worldwide. The versatility of the tomato, its flavor, and the large number of nutrients it provides to the consumer's

diet have allowed large amounts of tomato to be grown annually to meet commercial demand.

10.1.1.1 Generalities

Tomatoes are diverse in size and shape, but one of the most prevalent forms is elongated. The plants are covered by a layer that protects them from the outside environment, the cuticle. This is chemically heterogeneous and is composed of a lipid fraction, which is soluble in organic solvents, and another insoluble matrix, the cutin, which forms the cross-linking present in the cuticle. The cutin is a biopolyester formed mainly from the interesterification of the hydroxyalkanoic acids C16 and C18, which several studies indicate as a cross-linked amorphous polyester (Matas et al. 2004).

Tomatoes are a good source of bioactive molecules, especially carotenoids, of which lycopene stands out, which gives them not only high nutritional value but also beneficial properties for health, due to their great antioxidant activity, providing an important value added to the consumer's point of view (Colle et al. 2013). Lycopene is a compound of high interest in the food industry, when used as a dye, as well as in the pharmaceutical industry, for the prevention of cancer and the preparation of cosmetics (Matas et al. 2004). In addition to carotenoids, tomato contains a wide variety of antioxidants, such as vitamin A and C, β-carotene, and lycopene, among others. It is difficult to try to define natural antioxidants, but in general, the term refers to those substances that arise or can be extracted from the tissues of plants and animals and those that are formed during the cooking or processing of food compounds of origin vegetable or animal. Natural antioxidants are present in practically all plants, microorganisms, fungi, and even animal tissues (Zapata et al. 2007). The antioxidant content of tomatoes depends mainly on genetic factors, environmental factors, and maturation stages (Javanmardi and Kubota 2006).

10.1.1.2 Structure of the Fruit

The adult tomato is constituted, basically, by the pericarp, the placental tissue, and the seeds. The pericarp is composed of the external wall, the radical walls or septa that separate the locules, and the internal wall or columella. It originates from the wall of the ovary and consists of an exocarp or skin, a parenchymal mesocarp with vesicular bundles, and the endocarp constituted by a unicellular layer that surrounds the locules (Nuez 1995). The mesocarp of the external wall is composed mainly of parenchyma cells, which are larger in the central region and decrease along with the epidermis and the locules. The skin or exocarp consists of the outer epidermal layer, without stomata and practically without starch, and two to four layers of thick-walled hypodermic cells with collenchymal thickenings. The epidermis is covered by a thin cuticle that thickens as the fruit develops, and the cuticular area, 4–10 μm thick,

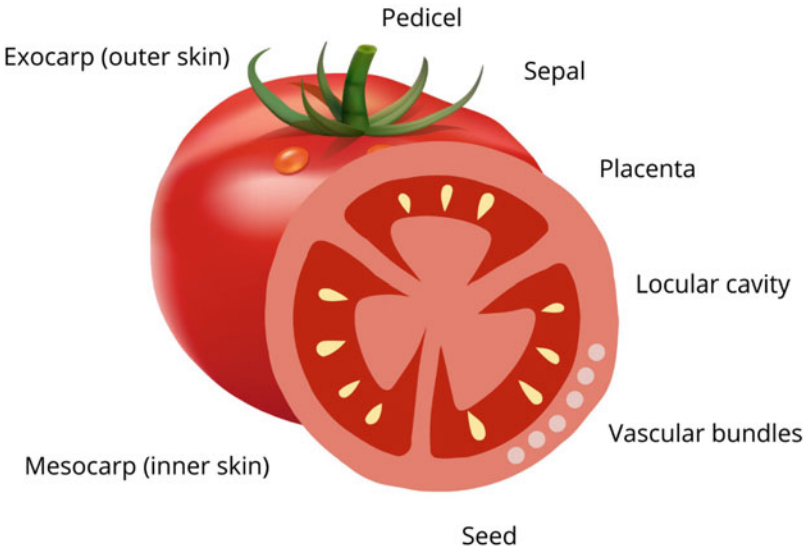

Fig. 10.1 Parts of tomato fruit

consists of two regions: a layer of chitin that covers the epidermal cells and a cuticular layer (Fig. 10.1) (Wilson and Sterling 1976).

10.1.1.3 General Composition

During the growth of the fruit, the content in dry matter, referred to as the fresh weight, decreases, due to the dilution produced by the rapid incorporation of water. The ovary contains 17% dry matter, and when the fruit begins to grow, it decreases progressively to stabilize at 20 days in 5–7% (Gustafson 1926). The accumulation of starch during the period of rapid growth seems to influence the final content of total soluble solids. The speed of accumulation of starch reaches a maximum at 20–25 days after anthesis and comes to assume 20% of the dry matter. The starch accumulates preferentially in the locular and placental tissue. The starch begins to hydrolyze when the growth of the fruit reaches the maximum, representing 1% of the dry matter in the mature green stage and 0.03% of the fresh weight in the ripe fruit (Vives 1984).

Sugars, mainly glucose and fructose, constitute 65% of the total soluble solids of mature fruit and range between 1.7 and 4% of the fresh weight of the fruit and the total soluble solids between 4 and 9% in commercial cultivars. The content in total soluble solids is inversely proportional to the yield in fruits and increases with the leaf surface. When the fruit begins to grow, the content of reducing sugars increases from 0.1% of the fresh weight of the ovary to 3.5% in the maturation. The content of sugars is greater in the walls than in the locules. Sucrose accounts for only 1% of the

dry matter at the beginning of maturation (Ho et al. 1983), but the metabolism of sucrose is important for fruit growth. After pollination, the content of reducing sugars and starch increases sharply, but that of sucrose decreases from 1 to 0.2% of the fresh weight of the fruit in 8 days. Although sucrose is the main assimilated imported by the fruit, the sucrose content is always low. Since the import speed of photo-assimilators is inversely proportional to the sucrose concentration in the fruit, the hydrolysis of sucrose may be regulating the import (Folquer 1976).

The content of organic acids increases during the development of the fruit and accumulates, preferably, in the locules. The main organic acids in tomatoes are malic and citric, which represent 13% of the dry matter. At the beginning of growth, malic acid is predominant, while citric acid only represents 25%. The pH of the ripe fruit juice ranges between 4 and 4.8 (Nuez 1995).

Nitrogen, phosphorus, and potassium account for more than 90% of the mineral content. During the development of the fruit, nitrogen and phosphorus decrease from 3% to 0.6% and from 2% to 0.4% of the dry matter, respectively, while potassium remains constant, at around 3%. Potassium represents 85% of the cations in the fruit, and its accumulation is proportional to that of dry matter. This relationship varies with the concentration of potassium in the nutrient solution and the culture conditions. The increase in potassium supply increases the acidity and color of the fruit. Potassium deficiency produces a shortening in the period of fruit growth and increases the maximum climacteric respiration (Nuez 1995).

10.1.1.4 Composition of Ripe Fruit

Although the fresh fruit is rich in vitamin C, the caloric power of the tomato is quite modest due to its low content of dry matter and fat. Both the water content and the other components depend on cultivation, nutrition, and cultivation conditions, among others.

10.1.1.5 Starch

Immature tomatoes have relatively high concentrations of starch that can exceed 1% of fresh weight but fall to 0.1% in red ripe fruits (Nuez 1995).

10.1.1.6 Sugars

Sugars constitute most of the soluble solids in commercial tomato varieties, with values of 1.5–4.5% of fresh weight, which is equivalent to 65% of total soluble solids. The most abundant free sugars are glucose and fructose, which are found in similar proportions. Sucrose, which is the main form of transport of photo-assimilators in leaves, does not usually exceed 0.1% of fresh weight, although some non-commercial species of the genus *Lycopersicon* contain large amounts of

sucrose and very little glucose and fructose. The content of sugars undergoes a sudden growth when the fruit reaches a yellowish color and gradually increases during ripening so that the premature harvest adversely affects the sugar content (Villarreal-Medina and Delgado-Villarreal, 1982). The shading, the decrease in the duration of the light, and the elimination of the leaves decrease the content of sugars (Nuez 1995).

10.1.1.7 Organic Acids

Organic acids are important not only because of their biological effects but also their effects on industrial food processes. The predominant acid is citric acid, followed by malic acid; other acids such as formic, acetic, and transaconitic are minor. Acidity is mainly concentrated in the locular cavity and is relatively low in the external mesocarp (Nuez 1995). The maximum acidity during ripening matches with the appearance of the pink color and then descends progressively. The acidity of the tomato, as well as the relationship between malic and citric, depends to a large extent on the cultivar.

10.1.1.8 Volatile Compounds

The volatile fraction of the tomato consists of more than 400 substances, among which are hydrocarbons, ethers, phenols, aldehydes, alcohols, ketones, esters, lactones, sulfur compounds, amines, and a wide range of heterocyclic molecules. The concentration of volatile reducing substances increases during the ripening of the fruit and is higher in open-air crops than in greenhouse crops. The ripening in the plant is preferable to the maturation post-recollection, and the storage in refrigeration produces fruits with an inferior aroma. The variety does not seem to affect the quantitative distribution of the volatile components of the tomato (Nuez 1995).

10.1.1.9 Pigments

The green color of immature tomatoes is due to chlorophyll. With the onset of maturation, chloroplasts begin to transform into chromoplasts, initially in the gelatinous placental tissue that surrounds the seeds and then in the pericarp from the distal to the peduncle (Galietta et al. 2005).

10.1.1.10 Lipids

The lipid content of tomatoes is very low, between 10 and 20 mg of unsaponifiable lipids per gram of dry matter (Galietta et al. 2005).

10.1.2 Worldwide Production of Tomato Fruit and By-Products

The versatility of the tomato fruit, its valuable nutritional composition, and the constant innovation in the framework of more sustainable agriculture have significantly increased the production and consumption of fresh tomatoes, as well as tomato byproducts, around the world. The tomato is then, after the potato, the most consumed fruit in the world, both fresh and after processing. The tomato is positioned as one of the most important vegetables due to the sown area that is intended for cultivation (both in an open field and in greenhouses) and the volume it occupies in the market of various countries, as well as its production value. This vegetable is grown and consumed throughout the world, being one of the main vegetable crops considered a primary food in many countries and cultures. It can be consumed fresh and directly from the crop or also cooked in different presentations. It is rich in various nutrients such as flavonoids, carotenoids, vitamins, fibers, and minerals, mainly. What makes it a very popular food for the benefits it generates in health is as an antioxidant, anticancer, cardioprotective, and antimicrobial (Oboh et al. 2015). In addition, the rich and fresh flavor of this berry generates a very high market opportunity. For this reason, its worldwide distribution is favored by the high demand for consumption of this vegetable and by the conditions of cultivation, storage, and distribution (Guo et al. 2020).

It is cultivated in all latitudes under very varied conditions (climates, production modes, etc.). Due to the characteristics of tomato plant growth, the highest production is generated in temperate zones with an average daily temperature ideal for growth ranging between 18 °C and 25 °C, and nocturne temperatures between 10 °C and 20 °C, near to the 40th parallels, mainly in the Northern hemisphere (Food and Agriculture Organization of the United Nations 2020b; Liadakis et al. 2022).

Tomato consumption has increased in recent years, which has led to the need to increase tomato crops throughout the world. The world production of fresh tomatoes has progressed regularly during the twentieth century and has increased considerably in recent decades. Between the beginning and end of 2012–2020, the volume of production of fresh tomatoes increased by more than 8 million tons (Anonymous 2021).

According to statistical data from the Food and Agriculture Organization (Food and Agriculture Organization of the United Nations 2021), around 186 million tons of fresh tomatoes were generated in 2020 worldwide (Food and Agriculture Organization of the United Nations 2021). These data indicate that there was a 9% increase in world production compared to 2017, when approximately 170 million tons of fresh tomatoes were generated worldwide (Fig. 10.2) (Zhengfei et al. 2017). The harvested area covered 5 million hectares globally (Fig. 10.3). The same that has remained almost the same as in 2015 when they increased only 10% until 2020; however, production did increase considerably from 176 million tons in 2015 to 186 million tons in 2020 (Fig. 10.2) (Food and Agriculture Organization of the United Nations 2021).

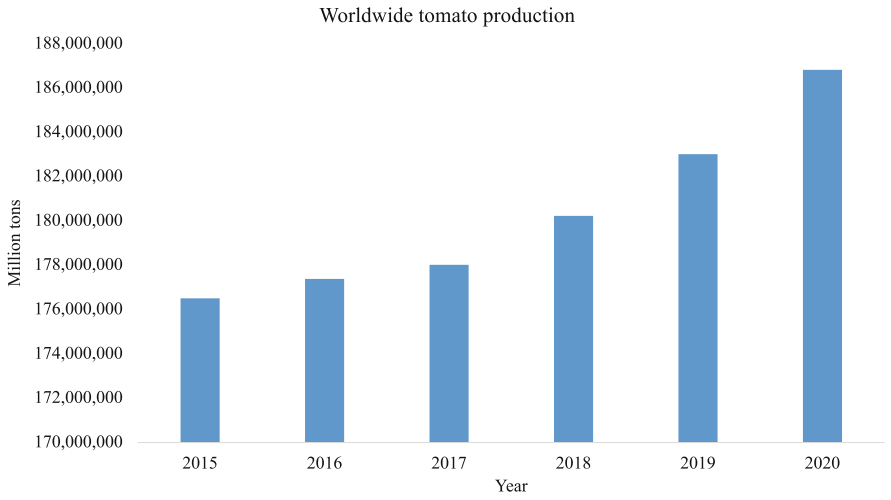

Fig. 10.2 World fresh tomato production from 2015 to 2020 (Food and Agriculture Organization of the United Nations 2021)

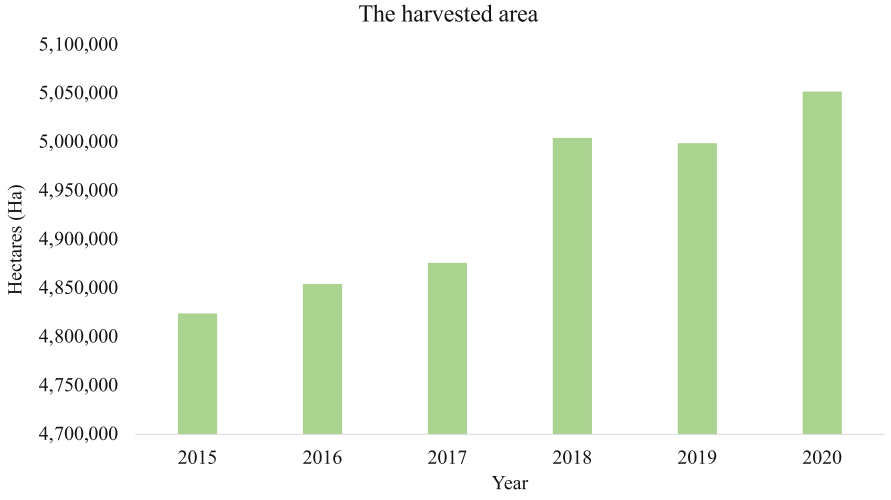

Fig. 10.3 Fresh tomato harvested area worldwide from 2015 to 2020 in hectares (Food and Agriculture Organization of the United Nations 2021)

Among the 16 countries that have produced 1 million tons or more, 6 are widely above 5 million tons. China is the world's largest tomato producer. This single country produces more than a third of the world's fresh tomato production; annual figures amount to 61.63 million tons. India, the United States, and Turkey remain on the list of main tomato producers with 19.18, 12.62, and 12.15 million tons, respectively. These countries are considered the largest producers supplying about

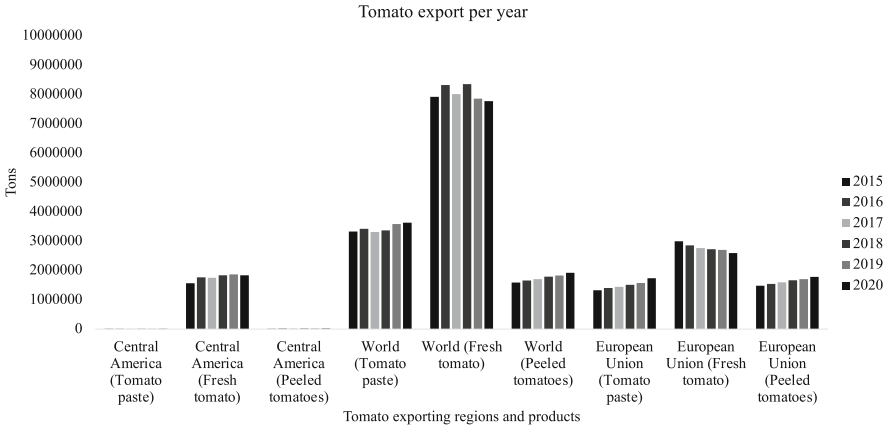

Fig. 10.4 Tomato production in tons for export worldwide, in Central America and the European Union, from 2015 to 2020, in various presentations of fresh tomato, peeled tomato and tomato paste

75% of the world's production of fresh tomatoes (Food and Agriculture Organization of the United Nations 2020a).

The production of fresh tomatoes in the European Union is also very high, approximately 16 million tons in 2020, being above Italy with 6 million tons, Spain with 4 million tons, and Portugal with approximately 1 million tons. The harvest area of these countries is 99 thousand hectares, 55 thousand hectares, and 15 thousand hectares, respectively.

In the American continent, the production of fresh tomatoes is greater in the United States with 12 million tons and Mexico and Brazil with approximately 4 million tons. In the least developed countries, tomato production is 4 million tons altogether (Fig. 10.4) (Food and Agriculture Organization of the United Nations 2021; Servicio de Información Agroalimentaria y Pesquera 2021).

All this tomato production has a very important economic impact worldwide and in a particular way in each country. Globally in 2020, 7 million tons of fresh tomatoes, almost 2 million peeled tomatoes, and almost 4 million of tomato paste were exported, generating an economic export value of $9.8 billion, $1.6 billion, and $3.4 billion (US$), respectively (Fig. 10.5). The countries that export the freshest tomatoes are Mexico, the Netherlands, and Spain, with values of 2 million tons and a value of $2.6 billion, 1 million tons with a value of $1.9 billion, and 700 thousand tons with a value of $1 billion (US $) in the year 2020, respectively (Food and Agriculture Organization of the United Nations 2021).

All these data indicate that the production of fresh tomato and its derived products such as pastes, purees, and sauces have a high impact on the world economy. It is considered one of the primary crops as a portion of basic food for the general population due to its beneficial properties for health and its fresh and rich flavor. This also indicates that it generates high amounts of waste, which, being biological, have the potential for application in various areas due to the compounds it contains and can be preserved.

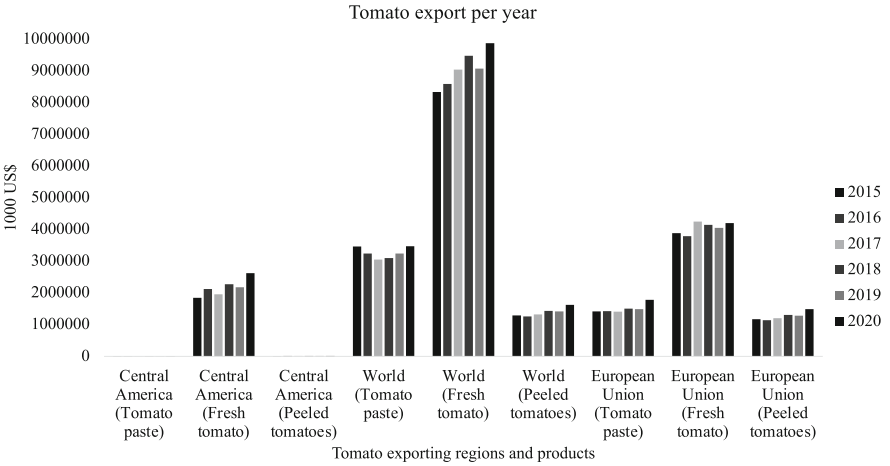

Fig. 10.5 Export data in miles of dollars of fresh tomato, peeled tomato and tomato paste worldwide, in Central America and in the European Union, from 2015 to 2020 (Food and Agriculture Organization of the United Nations 2021)

10.2 By-Products of Tomato Processing

Within vegetables, the tomato, which is consumed as a raw fruit or as a processed product, is the second most important horticultural crop in the world and one of the most important components of the Mediterranean diet (Strati and Oreopoulou 2014).

One of the areas of recycling that has taken great interest, in the context of food waste prevention and population growth, is the waste from different vegetable processing industries; these prevention strategies will lead to maximum benefits for industries, the environment, and consumers (Anal 2018). This type of waste obtained from the food industry contributes greatly to the environmental crisis that is being experienced by the generation of solid waste, of which horticulture produces 30 tons per hectare per year under greenhouse and 25 tons per hectare per year in the open air and at field level, tomatoes cultivation represents 30% of world horticultural production (Navia-Cuetia et al. 1976). In the tomato processing industry, approximately 8.5 tons of waste are generated worldwide each year (Szabo et al. 2018). During the transformation and processing of the tomato, a residue is produced, known as tomato pomace, which represents 3–5% by weight, is mainly composed of skins, seeds, and vascular tissues, and turns out to be rich in nutrients that can be used as a source of various bioproducts (Carillo et al. 2018).

Tomato waste is generated throughout the entire processed food production chain which starts from cultivation to industrial transformation. This includes selection and discard of poor-quality fruits; processing for various products results in enormous amounts of waste mainly as shell, seed, and pomace (Boccia et al. 2019).

The loss and waste of food in the tomato production chain, with values of approximately 79.8% of the waste produced in the supply chain, is represented by

edible parts and is made up of green, diseased, rotten, crushed, or broken tomatoes, mislabeling receipt errors and problems during product preparation, while the remaining part is represented by non-edible parts composed mainly of shells, seeds, and inert waste (Boccia et al. 2019). According to common processing industries, they produce tomato by-products, skin, seed, or pomace consisting mainly of skin, seeds, and a small amount of pulp which represent up to 5% of the whole tomato. These by-products are a source of valuable compounds: minerals, vitamins, dietary fibers, proteins, polyphenols, and carotenoids (Madia et al. 2021).

Tomato residues are an important source of natural carotenoids and phenolic substances, used as potential agents for the prevention of diseases related to oxidative stress; these compounds contribute to the nutritional value and affect its quality attributes (aroma, flavor, texture, and appearance) (Morand and Tomás-Barberán 2019; Veiga et al. 2020).

Industrial waste and by-products from the tomato field represent a valuable source of compounds due to their important nutraceutical potential, and therefore a good source of raw material for obtaining food ingredients and additives. These residues are a potential source for the extraction of phenolic compounds, highlighting the flavonoids: naringenin, catechin, and rutin (Paulino et al. 2020). Carotenoids constitute an important component of these by-products, among which we find lycopene, β-carotene, and lutein, predominantly in their trans configuration (Strati and Oreopoulou 2016). Caffeic acid is the most abundant phenolic acid and is found mainly in its conjugated forms; naringenin is the most abundant flavonoid and is found mainly in bound form in tomato residues (Perea-Domínguez et al. 2018).

Tomato pomace as mentioned above consists mainly of the peel and seed of the fruit; it is a material rich in lycopene, a phytochemical with antioxidant and chemopreventive properties (Zuorro et al. 2013). Speaking of lycopene, it is a compound with a high commercial value due to its great versatility in the market, finding it as a natural pigment and bioactive compound with functional properties; it can be used in nutraceuticals, cosmetics, pharmaceuticals, and as an ingredient in different foods and beverages (Urbonavičienė et al. 2021).

As we know, valuable bioactive components can be obtained from tomato residues, and be a source for the enrichment of foods or supplements (Kowalska et al. 2017) that have adequate physicochemical, microbiological, and nutritional quality to be used as a functional ingredient (Valle-Castillo et al. 2021) and generate new products, such as obtaining tomato seed oil rich in carotenoids and linoleic acid as the main fatty acid (Szabo et al. 2021). The use of waste from the tomato industry has great energy potential to produce bioethanol, not only giving this waste a nutritional twist but also the opportunity to develop viable and sustainable processes to produce biofuels (Suárez Reyes et al. 2020).

10.2.1 Shells and Skins

Food industries prefer the skin to be thick and rigid to facilitate the process, while consumers of fresh products prefer the skin to be thin and smooth to be able to eat them easily (Hetzroni et al. 2011).

Tomato peel has a high moisture content, and among the nutrients of this residue, it has a higher content of dietary fiber, followed by proteins and fats, and has a high antioxidant capacity, mainly attributed to a large amount of lycopene (Silva et al. 2019). This tomato processing residue is considered a source of bioactive compounds; the main phenolic compound present is rutin, followed by naringenin and lycopene (Navarro-González et al. 2011). Compared to tomato pomace, the main phenolic compound present is lycopene. The shell has a high nutritional value due to its content of essential amino acids and fatty acids, in addition to its high content of antioxidants such as flavonoids, phenolic acids, lycopene, ascorbic acid, and minerals (Se, Ca, Cu, Mn, and Zn), making the skin of tomatoes as a value-added ingredient in food products by improving the intake of natural antioxidants (Elbadrawy and Sello 2016).

The shell is rich in anhydrogalacturonic acid exceeding 60%, which indicates that it is a good source of pectin. Analysis of the sugars in tomato peel pectin revealed the presence of 6 neutral sugars (fucose, rhamnose, arabinose, galactose, glucose, and xylose) (Morales-Contreras et al. 2017).

One approach for the use of tomato peel is to enrich edible oils with carotenoids and lycopene, incorporating these derivatives into low-quality oils, such as refined olive oils, and obtaining new functional foods (Benakmoum et al. 2008).

10.2.2 Seeds

Europe produces more than 10 million tons to be processed; Italy, Spain, and Portugal are the main producers (Madia et al. 2021). The USA, Mexico, and Brazil are the main tomato producers in America; residues from the production of sauces, pastes, juices, puree, and other tomato products generate between 638,452 and 1,064,072 tons of residue each year; tomato seeds represent 60% of them (Maldonado-torres et al. 2020).

Tomato seeds have long been known to be a good source mainly of high nutritional oil or protein (Sato and Sakamura 1973; El-Tamimi et al. 1979).

According to Persia et al. (2003), tomato seeds are rich in three important components, total dietary fiber (34%), protein content (25%), and fat content (20%); the moisture content is already 10% and contains a high content of minerals (3%) composed by calcium and potassium. The protein content of tomato seeds is characterized by the presence of important amino acids, including Asp, Thr, Ser, Glu, Pro, Ala, Cys, Val, Met, Ile, Leu, Tyr, Phe, His, Lys, and Arg (Liadakis et al. 1995; Persia et al. 2003).

The total content of oil in tomato seeds is around 18–27% (Roy et al. 1994; Ouatmani et al. 2022); in that oil different compounds can be found as phenolic compounds, carotenoids, and fatty acids. Depending on the variety of tomatoes and the extraction treatment applied, the total phenolic compounds can reach quantities over 300 mg of gallic acid equivalent per 100 mL of oil; the total carotenoids content can be over 15 mg β-carotene per 100 mL of oil determined by UV-Vis spectroscopy at 450 nm, but achieving a High-Performance Liquid Chromatography Coupled with Diode Array detector analysis the sum of carotenoids can reach more than 45 mg/100 mL oil, founding mainly lutein, lycopene, and β-carotene (Szabo et al. 2021). About the fatty acids content, those compounds are around 75% of the total oil content, finding mainly oleic, linoleic, myristic, palmitic, palmitoleic, stearic, and elaidic acids (Gharbi et al. 2017).

Tomato seeds also have been used for animal feeding due to their protein level content improving fat content milk from cows or bigger size in sheep. Also, tomato seed powder has been used in bakery products like crackers and bread increasing protein content. The proteins in tomato seeds can have a nutraceutical effect mainly due to bioactive peptides derived from whole protein with physiological benefits like antidiabetic, anti-inflammatory, antihypertensive, and antioxidative, among others (Maldonado-torres et al. 2020). The bioactive peptides can be produced by the fermentative action of microorganisms like *Lactobacillus* sp., *Lactococcus lactis* subsp. *lactis*, *Lactococcus lactis* subsp. *lactis biovar diacetylactis*, *Lactococcus lactis* subsp. *cremoris*, *Leuconostoc mesenteroides* subsp. *cremoris*, and *Lactobacillus kefir*, among others (Mechmeche et al. 2018).

Other kinds of compounds that can be found in tomato seeds are saponins and flavonol glycosides (Takeda et al. 2021). These kinds of compounds confer foamy quality when agitated in water to their solutions or antioxidant properties, respectively.

Another potential use of tomato seed flour is as a complement of feed for small animals (Persia et al. 2003), but also as a source of demethylsterols (brassicasterol, campesterol, stigmasterol, beta-sitosterol, and D-avenasterol) with high antioxidant activities as demonstrated by (Małecka 2002).

However, tomato seeds have been poorly explored, and their use is very limited to cosmetic/pharma applications due to several health benefits and treats mild to severe skin diseases and dry hair.

10.2.3 Pulp, Paste, Puree

Tomato pulp is a small part of the tomato pomace (Kiralan and Ketenoglu 2022), a by-product obtained after processing this fruit in the food industry (Arbouche et al. 2021).

(Amón and Simmons 2017) reported that industrial tomato processing involves the concentration of tomato juice to produce paste and puree from the tomato pulp, but also, as the production of non-concentrated products such as diced or peeled

tomatoes. Generally, all concentrated tomato products can be rehydrated to produce puree, sauce, jam, or juice in subsequent processing steps.

Different valorization uses or applications for these by-products have been reported by (Kiralan and Ketenoglu 2022). Tomato waste can be generally re-evaluated as food ingredients and as animal feed, but also, can be used in non-food uses. Among the main applications for human food of tomato by-products are meat products, bakery products, edible oil, fermented cereals, and tomato-based products, while non-food uses are bio-oil and animal feed (Kiralan and Ketenoglu 2022).

When tomato pulp is a waste due to biological, environmental, mechanical, or processing conditions, it can be used to recover the protein and carbohydrate contents, but also pigments and alkaloids (Kramer and Kwee 1977).

Carotenoid extraction, particularly lycopene, from tomato waste is an attractive alternative (Baysal et al. 2000). However, if the utilization of tomato biomass is bioprocesses under the biorefinery concept, there is a great opportunity for the valorization of this agroindustrial residue. This has been a research topic of interest, and several reports on the influence of carotenoid extraction techniques have been published (Luengo et al. 2014b; Strati and Oreopoulou 2014; Stajčić et al. 2015; Strati et al. 2015; Trombino et al. 2021; Li et al. 2022a; Méndez-Carmona et al. 2022; Tiwari et al. 2022).

Carotenoids can be utilized in food colorants, functional food ingredients, dietary supplements, pharmaceuticals, and cosmetic products.

Other bioactive molecules such as phenolics, tools, terpenes, and sterols are also present in tomato waste. Such components are valuable for their biological activities and beneficial to human health (Kalogeropoulos et al. 2012).

Flavonoids and phenolic acids are potent bioactive due to the free radical scavenging activity and several potential health-promoting effects. Flavonols (quercetin, rutin-derivative) and flavanone (naringenin-derivative) are the major phenolic compounds found in these wastes (Ćetković et al. 2012). Tomato waste also contains hydroxycinnamic, ellagic, chlorogenic, salicylic, gallic, vanillic, coumaric, and syringic acids and rutin and myricetin in lower concentrations (Nour et al. 2018).

10.3 Methods for the Recovery of Bioactive Compounds

10.3.1 Technologies for Extraction and Recovery

10.3.1.1 Pulsed Electric Field

From 1950 to the beginning of the present century, the use of Pulsed Electric Fields (PEF) was an innovative mechanism to inactivate microorganisms based on its capability to the ripe membrane and because it suppressed the necessity to use thermic processing (Palaniappan et al. 1990; Vega-Mercado et al. 1996; Jeyamkondan et al. 1999). The first approaches to PEF as a tool for the obtention

of bioactive compounds from the plant were the description of its effects on plant tissue, evidencing that plant cell membranes raised their permeability after facing the treatment (Fincan and Dejmek 2002; Schultheiss et al. 2002). The extraction assisted by pulse electric fields of phytochemical compounds depends on the electroporation phenomenon, which means a pore formation on the membrane that allows the metabolites to break free from the cell's inner environment. This damage may be reversible (when the strength of the electric field does exceed drastically the defensive electric endurance of the cell) and irreversible (the cell is permanently damaged) depending on the characteristics of the PEFs. The liquid-solid extraction assisted by PEFs needs special equipment that comprehends a high-voltage pulse generator, a fluid-managing capable treatment chamber, and a system that allows monitoring and controlling the process, allowing a batch-based or a continuous extraction, depending on its specific additaments and conformation (Ranjha et al. 2021).

PEFs assisted extraction is a promising method for the obtention of a wide diversity of bioactive compounds like carotenoids, anthocyanins, betaines, and tocopherols, from fruits and vegetables, like grapes, peach, cinnamon, moringa, and tomato, among others (Ranjha et al. 2021). By treating lyophilized tomato fruit with mild-force PEFs (0.4–2.0 kV/cm, 5–30 monopolar pulses, the fruits were refrigerated after treatment), Vallverdú-Queralt and coworkers obtained a 36.58% rise in the total polyphenol content, 20.1% rise in lycopene content, a 44% higher hydrophilic antioxidant capacity, and a lipophilic antioxidant capacity 37% higher in the homogenate from treated fruits (Vallverdú-Queralt et al. 2012). On the other hand, Luengo and coworkers treated tomato peel and pulp with PEFs (3–7 kV/cm, 5–100^2 pulses) to improve the carotenoid extraction using a mixture of hexane/ethanol/acetone. This process reduced the proportion of hexane without affecting the yield (Luengo et al. 2014a). In more recent works, the treatment with PEFs (1, 3, or 5 kV/cm, 10–833 monopolar pulses) improved the lycopene yield and the antioxidant power of both acetone and ethyl lactate extracts from industrial tomato by-products (Pataro et al. 2020). Another study on industrial tomato processing tested a multi-step technique for the PEFs over tomatoes in different stages. This process comprehends three PEFs steps: the first over the whole fruit, the second on chopped tomato, and the third on juicing residues. In the last one, the extraction of lycopene was raised by 45% with mild-force PEFs (1–5 kV/cm, 0–-500 pulses). This treatment reduced the work needed to peel the whole tomato and the juice yield (Andreou et al. 2020). It is essential to say that combining PEFs (3.8 kV/cm, 600 monopolar pulses) with thermic treatment may produce a decrement in lycopene and b-carotene bioaccessibility, likely due to undefined chromoplasts membrane changes and interactions between the target compound and proteins, undoubtedly related to the structural complexity of the tomato fraction (Bot et al. 2018).

10.3.1.2 Enzymatic Extraction

Enzymatic extraction is considered an excellent strategy for revalorizing and managing food waste and agro-industrial residues because it is safe, green technology, and capable of generating and removing desirable industrial compounds. The efficiency during the enzymatic extraction process is influenced by several factors such as temperature, extraction time, pH, substrate availability (particle size and mass ratio), type of enzyme, type of fermentation, type of microorganism, and other factors that are selected according to the specific enzyme used (Barcelos et al. 2020; Caruso et al. 2020).

Enzymatic extraction of lycopene from tomato industrial waste and paste has been previously studied. Commercial enzymes preparations or enzymes produced by solid-state fermentation of *Fusarium solani pisi* were used to improve lycopene extraction from tomato by-products; the lycopene extraction was influenced by pH, temperature (50 °C), solid-to-enzyme ratio (1/30 w/v), and tomato by-product size (0.8–1.25 mm); this way, the lycopene recovery was higher with fungal fermentation than enzyme preparations (Azabou et al. 2016). Tomato pomace is abundant in bioactive such as lycopene, vitamins, phenols, and dietary fibers. The application of the homogenization combined with enzymatic hydrolysis over tomato pomace by-product showed that the lycopene yield raised 57% and 73% for soluble dietary fibers (Li et al. 2022b).

The food pigments as the carotenoids are contained in chromoplast, enzymatic process as biotechnological strategies can be helpful. This way, the development of a tailored enzyme-assisted extraction protocol was proposed to recover lycopene from unsold tomatoes; this protocol considered that the lycopene obtained would be stable and protected against oxidation. The tailored enzymatic strategies included a mix based on polygalacturonase, pectin lyase, cellulase, and xylanase, considering the polysaccharide composition of the tomato cell wall. Factors such as temperature, pH, enzymatic mix concentration, and processing time were analyzed; these ways were found that the temperature range was 45–55 °C, pH was 4.5–5.5, and the most recovery yield was obtained with the treatment of 25 U/g for 180 min. The tailored enzymatic process showed a yield of 4.30 ± 0.08 mg lycopene/kg of tomato contained in chromoplast from 5.43 ± 0.04 mg lycopene/kg tomato in total carotenoids (Lombardelli et al. 2020).

Modifications on structural, rheological, and functional properties of soluble dietary fibers from waste tomato peel have been reported.

This study was carried out to compare three different methods to improve fiber extraction: alkaline hydrogen peroxide (A-SDF), hydrochloric acid-ethanol (E-SDF), and enzymatic hydrolysis. The results showed that the fiber sample of the three methods had a lower molecular mass and zeta potential than the original soluble dietary fiber (O-SDF). However, A-SDF presented better gelling properties, the capacity for glucose absorption, and the capacity to bind to bile acids (Niu et al. 2018).

Another bioactive studied from the peel of pomace tomato is oleoresin. Enzymes such as polygalacturonase, pectin methylesterase, cellulose, and hemicellulase were evaluated. The production rate of oleoresin was 27 ± 1.8 mg/g of dry peel, which contained about 7% of lycopene (Zuorro et al. 2014).

In summary, enzymatic extractions have shown promising results in producing nutraceuticals, and desirable industrial compounds are a green biotechnology process and allow specific procedures.

10.3.1.3 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction is a fast and green extraction technology that had its commercial uses and beginnings in 1970. SFE is based on the solvent properties; in this sense, a supercritical fluid is obtained when the pressure and temperature of a simple fluid are taken above the critical point. Therefore, the solvation power of the fluid can be manipulated (figure SFE). SFE depends on several parameters such as solvent choice, temperature, pressure, extraction time, solvent flow rate, extraction time, and use of modifier (Konar et al. 2012; Parhi and Suresh 2013; Sharif et al. 2014).

The solvents used for SFE are carbon dioxide, nitrous oxide, ethane, propane, pentane, ammonia, fluoroform, sulfur hexafluoride, and water (Zougagh et al. 2004).

Supercritical fluid has gas-like viscosity, diffusivity, liquid-like density, dielectric constant, and solvating properties that can be modified by pressure and temperature (Knez et al. 2019). Supercritical fluid has a lower viscosity and higher diffusivity than the original fluid; therefore, supercritical fluid has a major capacity to penetrate porous from a solid material of the vegetal sample. Consequently, the mass transfer is increased, resulting in faster and better recoveries (Lang and Wai 2001).

Aniceto and coworkers reviewed the valorization of tomato residues by supercritical fluid extraction. They detected three principal aspects affecting the extraction of bioactive molecules from tomatoes. The first aspect is the tomato matrix (peel, seed, pulp, juice, pomace, variety, and maturity); the second aspect is the pretreatment (enzymatic, drying, milling), and the third is extraction conditions (pressure, temperature, cosolvent, flow rate, time). Their review showed that dried and powdered seed, skins, and pomace alone or in combinations are the vegetable sources most used, the pressure range used is 7–50 MPa, the temperature range was 30–100 °C, and some experiments had ethanol, water, and vegetable oil as cosolvent, and the carotenoids particularly lycopene, β-carotene, and tocopherols are the bioactive mainly obtained. Finally, the units for recovery of bioactive were heterogeneous, their results were reported with several units as mg/g, %, g/100 g, and mg/L, but yields in percentages are more homogeneous, with 22–100% concerning total carotenoids or bioactive selected (Aniceto et al. 2022).

Lycopene is the nutraceutical most studied from tomato juice and by-products, particularly skin. A response surface methodology with a central composite rotatable design was used to evaluate the lycopene content in dried tomatoes to define the extraction conditions using carbon dioxide as fluid and ethanol as a modifier. Factors

such as temperature (40–70 °C), pressure (25 and 45 MPa), and modifier concentration (5–15%) were analyzed. All factors influence all *trans*-lycopene extraction; although the modifier's effect was not significant individually, the concentration of the modifier showed a synergetic effect. The highest yield was 33 μg/g and was predicted at 62 °C, 45 MPa, and 14% temperature, pressure, and modifier concentrations (Kassama et al. 2008).

10.3.1.4 Microwave-Assisted Extraction (MAE)

The first application of the microwave-assisted extraction (MAE) technique in foods was in the determination and separation of pollutants like iodine and bromine compounds as well as thiophanate methyl and carbendazim residues from fungicides (Chen et al. 2007; Singh et al. 2007); this methodology has been applied since the late 1990s, acting as a side-tool for food safety (Letellier and Budzinski 1999; Camel 2001). At the same time, MAE combined with ultrasonic processing was used to improve the obtention of lycopene from tomatoes. This early report shows that when the ultrasound treatment of tomato paste is reinforced with microwaving, the lycopene recuperation increases from 89.4% to 97.4% compared to only the ultrasonic process (Barriada-Pereira et al. 2007).

The main objective of tomato processing with MAE, like many other techniques, is to improve the obtention of lycopene and other antioxidant phytochemicals. In the following years, several works appeared indicating the benefits of using MAE techniques to remove bioactive compounds from tomatoes. For example, Ho and coworkers assayed different combinations of running factors with tomato peel as raw material. They tested the effect of solvent ratio (hexane/ethyl acetate), solid-liquid ratio, power, and energy for microwave treatment (Ho et al. 2015), obtaining an optimized set of conditions using pure ethyl acetate as extraction solvent and obtained 13.592 mg of lycopene 100 g of raw material.

Pinela and coworkers performed another optimization process to improve the obtention of phenolic acids, flavonoids, and antioxidant compounds from ripened tomatoes treated by an MAE process. The study included processing time, temperature, ethanol concentration, and solid-liquid ratio as relevant factors in a 5-level Box-Behnken design. First, they determine the optimum global conditions as 20 min, 180 °C, 0% ethanol (only water), and 45 g/L obtaining raised values for all their dependent variables (Pinela et al. 2016).

A different work group found that the chosen solvent, besides temperature, significantly influenced the polyphenol yield from tomato peel waste discarded by the canning industry. They found that high temperatures (90 °C) raise the total phenols and flavonoids in the obtained extracts by about 2× concerning the low-temperature extraction (25 °C). Besides this, the authors reported that 50–70% ethanol is the best option for the extraction solvent (Bakić et al. 2019).

The wastes produced by the tomato industry contain a set of compounds that represent economic and technological interests. Nowadays, MAE represents a valuable option for processing tomato by-products. For example, this technique (90 °C,

9:1 ethanol/ethyl acetate ratio, 3 min, 1:20 solute-to-solvent ratio) helped to obtain 66.93% more lycopene from an industrial pomace waste than a standard acetone extraction, representing a higher recovery in a significantly smaller processing time (3 min vs. 6 h) (Chada et al. 2022). Ouatmani and coworkers treated tomato seeds from an industrial tomato pomace with MAE (600 W microwave power, 78.9 s, 0% ethanol fraction, 1:30 solute-to-solvent ratio). They obtained almost 22% more tomato seeds oil than extraction by stirring and the Soxhlet method, with a total phenol content of 4.8× and 1.8×, respectively (Ouatmani et al. 2022). Pectin is another component that may be obtained from tomato by-products. Lasunon and Sengkhamparn optimized pectin obtention from industrial tomato pomace by MAE (300 W, 10 min), obtaining a high concentration of galacturonic acid and lycopene. The combination with ultrasound raised the pectin yield but not the other substrates (Lasunon and Sengkhamparn 2022). These novel and exciting applications encapsulate the obtained compounds, including phenols, flavonoids, proteins, and glycoalkaloids, for preparing advanced ground cover films. These polyethylene-based materials seek to protect and improve conditions in cultivars. Using industrial tomato by-products for making functionalized ground cover films may fit the revalorization practice of tomato wastes in the frame of a circular economy (Panagiotopoulou et al. 2022).

10.3.1.5 Ultrasound-Assisted Extraction (UAE)

Based on the need to apply greener and more sustainable extraction processes, the UAE has shown interesting results in the separation of bioactive compounds present in organic waste, including waste generated in the tomato processing industry. The acoustic cavitation phenomenon that governs the UAE consists of the formation of bubbles caused by ultrasonic waves due to negative pressure. Said cavitation bubbles expand by the high ultrasonic intensity causing a violent collapse of the gas bubbles present in the solvent resulting in a noticeable increase in the rate of mass transfer from the matrix to the solvent (Trombino et al. 2021). Therefore, as it is a non-thermal technology, UAE is particularly effective for the extraction of thermolabile compounds such as carotenoids present in the tomato wastes and tomato fruit residues originating in the process of manufacturing products.

(Li et al. 2022a) studied the extraction of biologically active compounds contained in tomato residues (skin and seeds) recovered as waste from tomato processing (tomato sauce). In this study, the effect and the interdependences of the UAE parameters were evaluated. In this sense, parameters of relevance for the ultrasound technique were analyzed such as temperature, time, volume, liquid-solid ratio, amplitude, pulser duration, and their interaction. The best conditions allowed the production of an extract rich in properties of interest: total carotenoids of 1408 ± 14 μg lycopene equivalents/g, lycopene yield of 1536 ± 53 μg/g, 36.1 ± 0.9 μg trolox equivalents/g as antiradical power. Studies of this magnitude allow to know the impact of the operating conditions, their interactions, and the results of the extraction to the evaluation of the process variables, evidencing that it

is possible to improve the number of compounds highly sensitive to temperatures such as carotenoids present in tomato waste through green, sustainable, fast, safe, simple, and cost-effective technologies.

10.3.1.6 Solid-State Fermentation Assisted Extraction (SSFAE)

Solid-state fermentation (SSF) is defined as the fermentative process that involves solids in the absence or near absence presence of free water; however, the substrate must have enough moisture that contributes to the growth and metabolism of the microorganism (Pandey 2003). Extraction assisted by fermentation in the solid state is a bioprocess that allows the revaluation of agro-industrial wastes as sources of biologically active compounds. The application of this bioprocess as an extraction medium has been implemented using a wide variety of food waste from the food processing industry as support (Sadh et al. 2018; Šelo et al. 2021). SSFAE offers several advantages compared to traditional extraction methods because, in addition to being a highly environmentally friendly process, it is easy to implement, the production process involves low operating costs, higher concentrations of end products, and easy recovery of extracts (Pandey 2003; Chilakamarry et al. 2022).

In recent literature, SSFAE has not been used for the recovery of biologically active compounds of residual tomato and waste from the production of tomato by-products. However, SSF has been used with *Fusarium solani pisi* to produce raw enzymes which were used to improve the extraction of lycopene from tomato processing products that included mainly skin and seeds. The results of this study showed greater recovery of lycopene when the enzymes produced in SSF by *F. solani pisi* were used compared to pectinases and cellulase preparations. In addition, the antioxidant potential was increased in the treatments that SSF was implemented (Azabou et al. 2016).

10.3.2 Bioactive Compounds

Tomato represents a source of important nutrients and bioactive compounds for human health. It is rich in dietary fiber and sugars (59%), protein (18%), lipids (20%), and minerals (3%). The fiber is composed mainly of cellulose, lignin, hemicellulose, and pectic, while the sugar content is represented by glucose, fructose, xylose, galactose, mannose, arabinose, and uronic acids. Also, some volatile compounds have been identified including dimethylindole, dimethylbenzaldehyde, benzoic acid, β-cyclocitral, diethenyl-dimethyl- and camphenol linalyl acetate (Coelho et al. 2021).

Several scientific reports have demonstrated the rich bioactive composition of tomato fruit and processing by-products. Important bioactive compounds such as phenolic compounds, polyunsaturated fatty acids, carotenoids, and dietary fiber have been successfully extracted (Szabo et al. 2022). In this context, the positive effects of

certain phytomolecules of tomato on human health (particularly preventing some non-communicable diseases) have been demonstrated, the case of lycopene, which acts as a potent antioxidant against reactive oxygen species and prevents in humans (Szabo et al. 2021). The most important bioactive compounds contained in tomatoes of interest for human health are carotenoids. They are natural pigments responsible for the red color of the fruit. Carotenoids have outstanding antioxidant activities. The human being cannot synthesize these kinds of molecules; for this reason, the consumption of tomato among other sources is primordial and related to dietary habits to enhance the immune system and reduces the risk of degenerative diseases, particularly different cardiovascular diseases, cancer types, cataracts, and macular degeneration (Strati and Oreopoulou 2014). It should be noted that recent studies have reported that women with lower breast cancer risk have high plasma concentrations of β-carotene and α-carotene (Bakker et al. 2016), while the supplementation of lycopene is effective against oxidative stress-induced neurodegeneration and aging-related inflammatory (Martins et al. 2017). Also, carotenoids have provitamin A activity helping to improve the final shelf life and/or sensory properties of food products (Kowalska et al. 2017). Among all carotenoids, tomato contains predominantly lycopene, β-carotene, and lutein, which are fat-soluble pigments, a particular kind of vegetable lipid (Szabo et al. 2021).

Tomato is a rich source of polyunsaturated fatty acids (PUFAs), particularly linoleic acid (Szabo et al. 2019). These are cell membrane lipids needed to maintain the fluidity and some cell physiological functions, like regulation of blood pressure or cell signaling; however, like carotenoids, the human being cannot synthesize two essential PUFAs, linoleic acid and alpha-linolenic acid; for this reason, tomato is essential in the human diet. Tomato seeds also contain tocopherols, phytosterols, and phenolic compounds of importance in human health (Aslan and Aslan 2017).

Tomato lipids can be considered biological active constituents, being suitable for the food, pharma, and cosmetic industries.

Tomato contains several free and bounded phenolic compounds which act on the prevention of a large variety of diseases, mainly gallic acid, rutin, 4-hydroxybenzoic acid, *p*-coumaric acid, chlorogenic acid, sinapic acid, quercetin, naringenin, caffeoylchlorogenic acid, cryptochlorogenic acid, caffeic acid, homovanillic acid, glucoside, ferulic acid, vicenin, protocatechuic acid, coumaroylquinic acid, feruloylquinic acid, apigenin, and eriodictyol (Araújo-Rodrigues et al. 2021; Coelho et al. 2021; Višnjevec et al. 2021). Carotenoids, polyunsaturated fatty acids (PUFAs), and phenolic are present in tomato by-products that are useful not only in preservation but also in valorization of food by-products during industrial processing and environment friendly.

If we have in mind, that the tomato sector has been one of the most growing agricultural activities worldwide, with a higher production of 200 million tons in 2021, such sector faces the major issue of the discarding of food and by-products, mainly by environmental stressors, microbial attacks, small animal attacks, and bad or deficient pre and post-harvest conditions. The overproduction is also a way for the tomato industry to overcome the potential fruit losses involved in the process and the high percentage of tomatoes that do not reach market standards. More than 30% of

tomato production is lost due to one condition or another, which makes it urgent to develop strategies to value it as much as possible, and today there are ecotechnologies, biotechnologies, and strategies that will undoubtedly help achieve it (Robert et al. 2014; Food and Agriculture Organization of the United Nations 2020c; Laranjeira et al. 2022). Tomato processing is a global and large-scale manufacturing sector with important product loss (30% approx.). This fruit is very versatile and can be processed into many different products, such as sauces and soups (18%), pastes and jams (17%), kétchup and juices (35%), and others, using different strategies and technologies (Raiola et al. 2015).

Therefore, valorization of by-products makes the whole process cost-effective and beneficial. This waste is rich source of several nutrients and minerals (Carillo et al. 2018). The main challenge has been related to its high-water content and fast rotting (Løvdal et al. 2019) The other alternatives are to use this biomass as source of energy (Aybek and Üçok 2017), for animal feed, or as soil fertilizer (Carillo et al. 2018). Unused and left in field, green tomatoes are rich in glycoalkaloids such as tomatine. Tomatine comprises two molecules, ⍰-tomatine and dehydrotomatine, both exhibit antioxidant, anti-inflammatory, antibiotic, and anti-fungal properties. immune-stimulating, cardiovascular effects, several types of cancers (colon, breast, lung, and prostate). Therefore, thorough investigation about mechanism of action is required to ascertain its properties (Ohno 2020).

Tomato pomace on dry weight basis is a source of protein (20%), fat (12%), and dietary fibers (30%). Seeds also contain sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), and other elements.

Tomato pomace also contains carotenoid-rich oleoresins. Oleoresins are a combination of pigments, fatty acids, fats, sterols, flavor compounds, and others that are usually extracted by successive conventional solvent extraction methods (Laranjeira et al. 2022). Oleoresins usually contain concentrates of active fractions; the aroma and flavor constituted by essential oil and resins are promptly absorbed in the organism and act as powerful antioxidants. These can be used in food and pharmaceutical industries for color, flavor, and other chemical properties (Rizk et al. 2014).

In conclusion, tomato's value added by-products can be used as natural antioxidants, preservatives, colorants, and functional food ingredients along with pharmaceutical and cosmetic applications (the United States Environmental Protection Agency (n.d.)).

10.4 Conclusions

The evident population growth brings with it an increase in the amount of food needed to meet population demands. Tomato is one of the fruits of greater consumption and production worldwide. It is considered a vegetable of high nutritional value. The large waste generated both in the production and transport chain of the tomato and in the processing industry for the processing of by-products offers an area of opportunity to revalue these valuable wastes because they are rich in bioactive

compounds, such is the case of carotenoids, phytosterols, and oleoresins, in addition to numerous micronutrients, which can be recovered through different extraction technologies. Procedures to increase the quantity and quality of compounds recovered from these wastes through conventional methodologies continue to be improved. However, it is essential to formulate strategies that allow the conservation of these compounds. The population's interest in consuming food and functional products that offer a plus in consumer health continues to rise; it is for this reason that the pharmaceutical and food area occupies an important place of application for compounds extracted from food waste such as tomatoes.

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Chapter 11
Sustainable Utilization of Tea Waste

Banhisikha Debnath and Mihir Kumar Purkait

Abstract Due to the growing demand all over the globe, the production of tea has increased drastically over the previous decades, which in turn resulted in the generation of massive amounts tea wastes that include the discarded leaves, stems, and buds of tea plants. Both the industrial tea processing wastes and domestic waste tea residues are imposing significant threats to our environment because of their inappropriate management. Therefore, utilization of tea waste is extremely necessary to minimize its negative impacts on the environment and also to help the tea factories in overcoming the challenges they usually face in handling such huge quantities of wastes. Tea waste being rich in polyphenolic constituents can be used successfully for the synthesis of bioactive compounds with medicinal importance. Factory tea wastes as well as household spent tea leaves are promising sources of different value-added products such as activated carbon, biochar, crystalline cellulose derivatives, metallic nanoparticles, biodegradable plastics, etc. Tea waste itself and also many tea waste-derived products can be utilized successfully for environmental remediation purpose, bioenergy generation, storage of energy, sustainable construction, environment-friendly packaging, and so on. This present book chapter presents the status of research on the utilization of tea wastes in different fields. With respect to that, the effectiveness of waste tea leaves for the treatment of both wastewater and drinking water, remediation of soil and air, and production of gaseous and liquid biofuel are evaluated. Further, electrochemical performance in energy storing systems and various other emerging applications of waste tea is elaborated in details.

Keywords Polyphenols · Activated carbon · Biochar · Adsorption · Bioenergy · Heavy metals

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11.1 Introduction

Tea is a well-known non-alcoholic beverage which is consumed extensively all over the world. Tea offers several amazing beneficial effects on human health which are the reason behind its widespread popularity. Anticancer, antidiabetic, anti-obesity, immune-modulatory, antivirus, anti-inflammatory, neuro-protective, antihypertensive, and cardiovascular preventive are some of the health benefits provided by tea. Tea also acts as a stimulant and refreshing agent. It is estimated somewhere in between 18 and 20 billion cups of tea are consumed everyday around the world. Tea alone equals to the sum of consumption of coffee, chocolates, soft drinks, and alcohol. Tea consumption was about 35 L per capita in the year 2018, holding the second position after drinking water, and by 2021 it was expected to rise up to 37.7 L (Debnath et al. 2021b; Xu et al. 2021). In 2020, the amount of tea consumption in the world was around 6.3 million metric tons, which is likely to grow up to 7.4 million metric tons by the year 2025. Nowadays, different tea-derived products are also becoming highly popular, for instance, bottled tea drinks, tea extracts, instant tea powder, ready-to-drink catechins, tea seed oil, etc. The ever-increasing demand of tea has led to a massive rise in tea production, which otherwise results in the generation of enormous quantities of tea waste (TW). During the processing of tea production in the factories, huge amounts of by-products such as discarded leaves, buds, and pruned stems are generated as wastes. There is no proper management available for these wastes, and they are usually dumped in landfills or incinerated causing a number of environmental problems. Besides, the residual leaves left after making tea infusion are considered as domestic tea waste, which increases the environmental load further since they are also burnt or disposed in landfills without any treatment. As the tea wastes are difficult to degrade, different environmental issues may arise like pollution of soil, water, and air (Chowdhury et al. 2016; Zheng et al. 2017; Debnath et al. 2022).

11.1.1 Current Scenario of Tea and Tea Waste Production

Tea has a long history of consumption since 1500 BC. It originated in the Yunnan province of China, and earlier it was used as a medicinal beverage. The infusion of tea is produced from the leaves of *Camellia sinensis* plant, and its harvesting process significantly effects the resulting product (Fig. 11.1). Numerous varieties of tea are available among which the major four main types are green, black, oolong, and white tea; all of them are made from the same plant. The largest tea market in the world belongs to China, with a value of over 78 billion US dollars. In 2020, the value of worldwide tea market amounted for around 200 billion US dollars and was estimated to reach over 318 billion US dollars by 2025. China, India, Kenya, Indonesia, and Sri Lanka are the major tea manufacturing countries of the world, among which the

Fig. 11.1 Tea plantation. (Source: https://www.fao.org/markets-and-trade/commodities/tea/en, accessed on 12/07/2022)

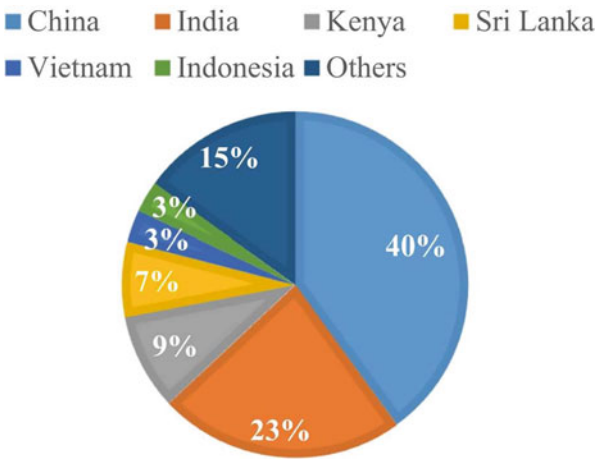

Fig. 11.2 Top tea manufacturing countries and their percentage share in global tea production. (From Debnath et al. (2021b))

Asian countries of China and India hold the first and second position, respectively (https://www.statista.com, as on 12/07/2022).

The Food and Agricultural Organization of the United Nation estimated that the global production of tea (black, green, instant, and other) has increased by an annual rate of 3.5% over the last decade and reached 6.29 million tons in the year 2020, which was mostly contributed by China. Green tea manufacturing is expected to grow almost twofold (from 1.5 million tons in 2017 to 3.6 million tons in 2027) in the current decade. In 2020, China produced approximately 2.93 million tons of tea (https://www.fao.org, as on 12/07/2022). The percentage share of the top tea producing countries in the total worldwide tea production is illustrated in Fig. 11.2. From the figure it can be seen that, the contribution of China is about 40% of the global tea production, while India shares nearly 23%. According to the annual bulletin of statistics published in 2020 by International Tea Committee, the total amount of tea produced worldwide in 2019 is around 6.1 million tons (Debnath et al. 2021b).

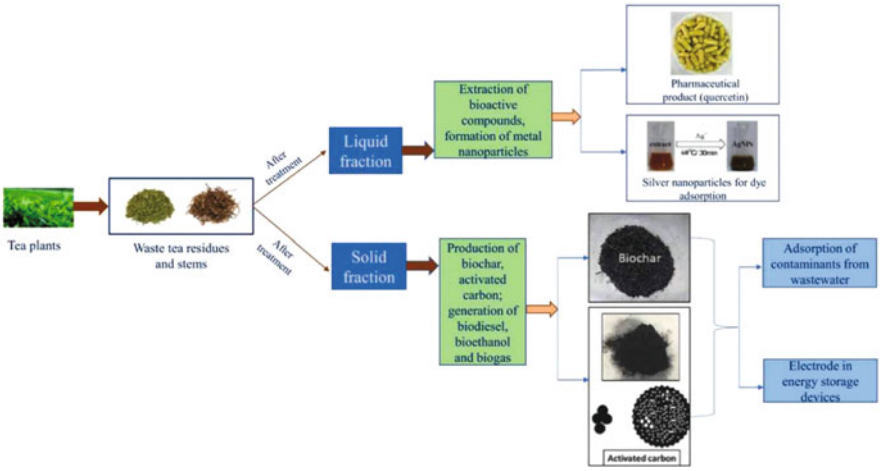

Fig. 11.3 Many ways of utilizing of tea waste in different fields. (From Debnath et al. (2021b))

India has around 5,79,000 ha area under tea cultivation, and close to 8,57,000 tons of tea is produced annually. Consequently, the wastes generated by the tea factories amount for 1,90,400 tons approximately (Basumatary et al. 2018). According to the reports of Tea Board of India, the total tea production in India in the financial year of 2020–2021 was near about 283 million kg, which was mainly driven by Assam and West Bengal. Tea production in Assam amounted to 626.2 million kg, while 396.1 million kg was produced by West Bengal in that year. The Tea Board of India has set the guideline for tea production to follow the clause no. 8 of the Tea Waste (Control) Order, 1959, that states there should be a minimum volume ratio of 2:100 kg in between wasted tea and produced tea, after performing the various processing operations on the tea shoots (consisting of buds and leaves) (https://www.teaboard.gov.in, accessed on 12/07/2022). According to this rule, the estimated generation of tea wastes from the Indian tea factories in the fiscal year of 2020–2021 (when 1283 million kg tea was produced) would have exceeded 25 million kg. Dumping such huge amounts of wastes will cause severe environmental pollution, and at the same time the tea factories are also facing major challenges in handling these wastes. Therefore, utilization of tea wastes is a need of the hour to mitigate these issues in a sustainable way. A schematic diagram of utilization of tea wastes in different fields is shown in Fig. 11.3.

11.1.2 Composition of Tea and Tea Waste

Tea is composed of numerous bioactive compounds that include polyphenols (catechins, flavonoids, proanthocyanidins), alkaloids (caffeine, theobromine, theophylline), polysaccharides, methylxanthines, minerals, vitamins, terpenoids, protein or

free amino acids, tannins, etc. (Tang et al. 2019; Shang et al. 2021). Tea waste generally has components similar to those of regular tea and the quantities are also close. The basic structure of tea waste is lignocellulosic that is made up of lignin, hemicellulose, cellulose, phenolic compounds, and so on (Sui et al. 2019; Debnath et al. 2021b). Both the tea processing wastes, i.e., pruned tea leaves, stems, and buds, and also the spent or brewed tea leaves left after making tea infusion contain substantial amounts of cellulose, lignin, hemicellulose, and also bioactive substances like polyphenols, polysaccharides, and proteins. The constituents of TW are rich in functional groups including hydroxyl, carboxyl, oxyl, phenolic hydroxyl, and also oxygen containing groups (Guo et al. 2021). The chemical composition of tea largely depends on its type. The major components of tea are flavonoids, consisting of around 20–30% of the chemical composition dry weight of tea. The key flavonoids present in tea are flavan-3-ols, also known as catechins. Epigallocatechin-3-gallate (EGCG), epicatechin-3-gallate (ECG), epigallocatechin (EGC), and epicatechin (EC) are four major catechins that constitute almost 90% of total catechin fraction. EGCG accounts for 48–55% of total tea flavonoids. Other types of flavonoids such as flavonols (quercetin, myricetin, kaempferol) are also present in tea leaves. Alkaloids (caffeine, theobromine) and phenolic acids are other important ingredients of tea. Black tea contains 2–5% (dry weight basis) of caffeine, while green tea has caffeine around 3% of its dry weight. The different types of tea contain different quantities of catechins, based on their oxidation degrees. Green tea refers to non-oxidized fresh tea leaves, oolong tea is semi-fermented made by partially oxidizing the tea leaves, and black tea is completely oxidized/fermented. During the fermentation of oolong and black tea, the catechins in the leaves are oxidized and dimerized to form theaflavins, while polymerized to thearubigins and theabrownings. Hence, the amounts of catechin are less in black or oolong tea as compared to green tea (Debnath et al. 2021b; Salman et al. 2022).

11.2 Extraction of Bioactive Antioxidant Compounds from Waste Tea

Different bioactive compounds can be extracted from tea waste like polyphenols, flavonoids, catechin, caffeine, etc. Polyphenols are mainly associated with the antioxidant activities of tea waste. Extraction of spent black tea using ethanol at 1:25 (solid/solvent) ratio under shaking at ambient temperature for 24 h can extract high levels of total phenolic compounds amounting for 152.87 mg gallic acid equivalent (GAE)/g and total flavonoid content as high as 47.40 mg catechin/g of black tea waste (Abdeltaif et al. 2018). Subcritical solvent extraction of brewed black TW using 71% concentration of ethanol (at 1:20 solid/solvent ratio, 2 MPa pressure, 180 °C temperature, under constant agitation for 10 min) gives a significantly high total polyphenols yield of 126.89 mg GAE/g of spent black tea. When the TW extract was encapsulated with a blend of pectin and sodium caseinate (1:1 ratio), an

amorphous powder was produced with the ability of 94.28% phenolic retention for storage at 45 °C for 40 days. The black TW extract-based microencapsulates can be used in different food systems for increasing their antioxidant capacity (Rajapaksha and Shimizu 2020). In order to intensify the extraction of bioactive compounds from tea waste and enhance their antioxidant properties, tea wastes can be treated with steam explosion to modify their physicochemical features. It has been observed that steam explosion can alter the composition of cell wall, damage and restructure the porous matrix of TW. Thus, it increases the solubility, diffusion, and extraction efficiency of the active constituents. Steam explosion could improve the solubility of factory tea waste by around 22.40% and thereby increase the extraction yields of polyphenols, caffeine, and saponin by 15.50, 14.10, and 28.80%, respectively. Steam explosion also improved the antioxidant capacity of the TW extract by around 20%, including OH, O_2 radical scavenging activity and ferric reducing antioxidant power (Sui et al. 2019).

11.3 Application of Tea Waste and Tea Waste-Derived Value-Added Products in the Environmental Sector

The acceleration of urbanization across the world may be attributed to the simultaneous rise in the world's population and economic growth. Despite the fact that industrialization and urbanization brought about a number of favorable benefits, they also resulted in a great deal of unintended consequences, such as environmental pollutions. There is a long-term deterioration in natural water quality in urban–rural expanding marginal areas owing to the discharge of industrial effluents as well as domestic sewage by the residents due to backward infrastructure construction. One of the most major difficulties that have long plagued human and animal existence is contamination of water with hazardous compounds like heavy metal ions, organic dyes, pesticides, herbicides, and medications. Such hazardous contaminants have been adsorbed, filtrated, separated, or removed from aqueous solutions using a variety of processes, including electrocoagulation, membrane filtration, ion exchange, chemical precipitation, and adsorption utilizing various materials, among which adsorption is the easiest, simplest, and mostly applied technique (Ghosh et al. 2011; Changmai et al. 2018; Singh et al. 2019).

Activated carbon (AC) is the most common adsorbent with very high adsorption efficiency towards several pollutants, but the conventional ACs are highly expensive and difficult to be recovered from aqueous solution post-adsorption. Therefore, bio-sorbents have received much attention in the present era owing to the abundant and easy availability, low-cost, and high adsorption efficacy of the biobased materials. Tea waste shows tremendous potential for application in the environmental sector as adsorbents (Debnath et al. 2020, 2022). A wide variety of pollutants can be effectively removed from aqueous medium by using waste tea leaves such as toxic dyes (Foroughi-Dahr et al. 2015), heavy metal ions (Malakahmad et al. 2016; Çelebi

et al. 2020), pharmaceutical pollutants (Patil et al. 2019), organic pollutants (Gupta and Balomajumder 2015), and so on. The waste leaves of green, black, and rooibos tea (5 days sun-drying followed by 2 days oven-drying at 100 °C) showed removal efficiencies of 83, 88, and 74%, respectively, for hexavalent chromium (Çelebi 2020). Brewed tea waste was successfully utilized for removing several other heavy metals including cadmium, zinc, nickel, lead and showed maximum adsorption capacities of 2.47, 1.46, 1.16, and 1.19 mg/g, respectively (Çelebi et al. 2020). Mixed type of tea waste after oven-drying at 60 °C for a period of 3 days displayed an adsorption capacity higher than 94 mg/g for hexavalent chromium, and the adsorbent could be recycled up to 4 times without any significant reduction of the efficiency. The adsorption of Cr(VI) onto the dried TW followed pseudo-second-order kinetics and Freundlich isotherm model. The excellent adsorption of Cr(VI) by the TW was attributed to carbon and oxygen-containing functional groups present on surface of the adsorbent (Cherdchoo et al. 2019). Domestic spent tea waste, subsequently dried for 2 days in sunlight and then at 85 °C in oven for 24 h, removed Cr (VI) from the effluents of tannery industry with around 97% efficiency. The adsorbent also showed good removal efficiencies for COD, total solids (TS), as well as total dissolved solids (TDS) from tanning industry wastewater, amounting for almost 74.8, 71, and 55%, respectively (Nigam et al. 2019). An adsorbent synthesized by drying spent tea leaves at 60 °C for 24 h could remove a pharmaceutical contaminant, named hydralazine hydrochloride, from aqueous solution with 74% efficiency, while the maximum pollutant adsorption capacity was 131.6 mg/g. The dried TW also successfully recovered the contaminant from real wastewaters of hospital and river. Waste tea residue possesses mesoporous structure, which along with the surface functional groups are ascribed to this pharmaceutical adsorption (Patil et al. 2019). TW acts as a highly functional adsorbent with outstanding removal of various types of pollutants. The interaction between the abundant functional groups such as hydroxyl, carboxylic, phenolic, amine, etc. contained in the components of TW and the ions of dyes, heavy metals, pharmaceuticals, or other pollutants via complex formation, ion exchange, electrostatic attraction, and π-π interaction attributes to their removal. Being an agricultural waste with no economic value, tea waste can be considered as a cheap and environment-friendly adsorbent for the treatment of contaminated water. Apart from the raw tea wastes, several other adsorbent materials can be derived from waste tea residues like activated carbon, biochar, metallic nanoparticles, hydrogels, etc., which also show promising potential to be employed in the environmental clean-up purpose. These tea waste-derived products generally exhibit greater adsorption efficiencies for various contaminants as compared to that of the pristine or unmodified TW (Çelebi 2020; Nie et al. 2021; Debnath et al. 2022).

Sometimes tea waste is modified using chemicals in order to enhance the adsorption performance. Chemical treatment improves the porous structure and enlarges the specific surface of the prepared adsorbent, thus leading to increased adsorption efficiency. Among the various types of chemical modification methods, treatment with alkali is mostly used for modifying the surface of lignocellulosic wastes, because alkali has the ability to considerably change the molecular structure as

well as the morphology of cellulose, and thereby increases the reactivity and ion exchange capacity of the adsorbent through the introduction of various active functional groups including -COOH (carboxyl), -OH (hydroxyl), and -C=O (carbonyl) (Kabir et al. 2021; Debnath et al. 2022). An alkali modified adsorbent was synthesized by treating dried TW with sodium hydroxide for 35 min, then washing with deionized water followed by drying at 100 °C temperature for 18 h. Around 96% removal of Cr(VI) was achieved using the modified adsorbent, whereas the pristine tea waste had 83.9% efficiency. An excellent Cr(VI) adsorption capability of 158.73 mg/g could be attained using the alkali treated TW. Chromium adsorption onto the alkali modified TW was a monolayer adsorption process, chemisorption being the predominant rate-determining step (Kabir et al. 2021). NaOH modified TW shows outstanding adsorption capacity (461 mg/g) for methylene blue (MB) dye. The primary mechanisms behind the adsorption of MB by NaOH modified TW involves complexation and ion exchange. The various components of TW contain methyl esters that change into carboxylate ligands by NaOH; as a result the dye-binding capacity of the modified TW gets increased because the -COOH groups can easily interact with the cations of methylene blue (Pirbazari et al. 2014). Modification using acid can also improve the surface area and pore volume of tea waste, contributing more active sites for the adsorption of pollutants. Domestic waste tea residues treated with concentrated H_2SO_4 exhibited a superb removal efficiency amounted to be 95%, for the anionic dye Eriochrome Black-T (EBT), while maximum EBT uptake capacity was found to be more than 150 mg/g. Langmuir isotherm suitably explained the adsorption equilibrium indicating monolayer adsorption of EBT onto the adsorbent surface. The adsorption kinetics obeyed pseudo-second-order model suggesting chemisorption via several mechanisms including hydrophobic interaction, π-π stacking, electrostatic attraction, and Van der Waals interaction (Bansal et al. 2020). Another effective method for the surface modification of tea waste is sulfonation. Sulfonation functionalizes the TW surface by creating negative charge, which is favorable for the adsorption of cationic pollutants. It was observed that sulfonation of powdered tea waste (treatment with concentrated H_2SO_4 at 70 °C for 4 h under continuous stirring) results in extraordinarily high adsorption capacities for cationic methylene blue (1007 mg/g), hexavalent chromium (438 mg/g), and tetracycline (381 mg/g). The adsorption of all these three pollutants by sulfonated TW have favorable, spontaneous, and endothermic nature (Ahsan et al. 2018).

11.3.1 Production of Porous Activated Carbon and Biochar

Activated carbon and biochar are porous carbon-rich materials, which have immense application potential towards the removal of different kinds of pollutants owing to their porous matrix, extensive specific surface, abundant surface functional groups, high ion exchange ability, non-toxic nature, outstanding adsorption efficiency, and rapid adsorption rate (Ghaedi et al. 2011; Taghizadeh et al. 2013; Meng et al. 2018).

Owing to the abundant amounts of carbon content in the various components of TW, it is found to be a suitable precursor for the synthesis of low-cost AC and biochar that can be successfully utilized for the remediation of the environment. The frequently adopted methods for producing activated carbon and biochar employing waste tea are listed in Table 11.1.

From the table it can be observed that two methods are available for the synthesis of activated carbons employing tea waste, namely, chemical activation (Kan et al. 2017; Akbayrak et al. 2020; Tuli et al. 2020) and physical activation (Fadhil et al. 2012; Zhou et al. 2018). Chemical activation method involves initial impregnation of the raw TW using various activating agents like $ZnCl_2$, H_3PO_4, KOH, and NaOH and its subsequent carbonization under inert atmosphere. In physical activation, the raw material is initially carbonized at elevated temperatures in the range of 500–600 °C in an inert atmospheric condition followed by activation of the prepared char at higher temperatures around 800 °C in presence of carbon dioxide or steam or a mixture of these two. Both of these methods are useful to produce porous materials having large surface area (Tuli et al. 2020; Debnath et al. 2022). The yield of AC is more in chemical activation than that of physical activation. Also, the chemically activated carbons seem to have better properties as compared to those of the AC synthesized by physical activation. Chemical activation method has many advantages including lower temperature, less time, and energy requirement, but higher consumption of expensive chemicals makes it a costly method. On the contrary, physical activation doesn't require any chemical neutralization of the prepared ACs, and hence it involves minimum pollution and less process cost. Furthermore, in this method the formation of micro-pores on the synthesized ACs can be controlled by optimizing the carbonization stage (Hussain et al. 2018). An advanced technique has been developed for producing AC from TW through combined physical and microwave activation. For that, waste tea leaves were firstly washed with distilled water and sun-dried for 24 h. Afterwards, the dried wastes heated gradually from ambient temperature to the desired carbonization temperature in a muffle furnace, with a heating rate of 4 °C/min. The char obtained was subjected to further activation in a microwave oven at 800 W power and 2450 MHz frequency, for 5 min (Dutta et al. 2015). AC prepared by co-carbonization of spent tea waste along with waste truck tyres has been found to possess comparable properties as the commercially available ACs. The blend of waste tyres and spent at 3:1 ratio, activated with $ZnCl_2$, provided the highest yield of AC (Guclu et al. 2021).

Biochar is prepared from TW by two different thermochemical conversion techniques: hydrothermal carbonization (Guo et al. 2019, 2020a) and pyrolysis (Borgohain et al. 2020; Azeem et al. 2021). Pyrolysis refers to the thermal degradation of biomass in an oxygen-free or oxygen-lack environment at temperatures in between 400 and 700 °C. The high temperature used in this method breaks down the different constituents of waste tea like cellulose, hemicellulose, and lignin. On the other hand, hydrothermal carbonization (HTC) method is carried out in moderate temperatures ranging from 180 to 250 °C and pressure in the range of 2–6 MPa, with water in subcritical condition (Kumar et al. 2020). It has been observed that biochar produced via pyrolysis possesses higher surface area than that synthesized by HTC.

Table 11.1 Activated carbon and biochar production utilizing tea waste

Precursor/ starting material	Porous carbonaceous product	Method of synthesis	Experimental conditions	Yield of adsorbent material (%)	References
Spent tea waste after making tea	Activated carbon	Chemical activation using H_3PO_4, KOH, and $ZnCl_2$	Impregnation of fine tea waste powder with and 70 wt.% of H_3PO_4, KOH, and $ZnCl_2$ separately at a ratio of 3.5:1 in ambient condition for 24 h, followed by carbonization in furnace at 500 °C temperature for 2 h, heating at a rate of 10 °C/min	–	Tuli et al. (2020)
Waste woody parts of tea	Activated carbon	Chemical activation using H_3PO_4	Activation with 20 wt.% H_3PO_4 at 85 °C temperature for 5 h under stirring and carbonization at temperatures of 300–800 °C, with a heating rate of 10 °C/min under nitrogen atmosphere flowing at a rate of 100 mL/min	–	Akbayrak et al. (2020)
Waste leaves of tea	Activated carbon	Physical activation using steam	At first, carbonization of TW at 450 °C for 30 min, at 5 °C/min heating rate, and nitrogen flowing at a rate of 100 mL/min. Thereafter, physical activation at variable temperatures 700–900 °C for 0.5–1.5 h, using steam generated by pumping water at 0.075 g/min flow rate	24 at 700 °C activation temperature and 18 at 900 °C	Zhou et al. (2018)
Spent tea waste	Activated carbon		Carbonization of tea waste in an	27	Fadhil et al. (2012)

(continued)

Table 11.1 (continued)

Precursor/ starting material	Porous carbonaceous product	Method of synthesis	Experimental conditions	Yield of adsorbent material (%)	References
		Physical activation using steam	electric furnace at 600 °C temperature for 2 h under gradual steam flow		
Spent tea residues left after making tea	Activated carbon	Chemical activation using H_3PO_4	Impregnating TW with 40 wt.% H_3PO_4 solution at an impregnation ratio of 1:1.5, followed by carbonization at 450 °C for 1 h, under nitrogen, air, and steam atmosphere	34.8 in presence of N_2, 27.6 in air, and 38.9 in steam	Kan et al. (2017)
Waste tea stems	Biochar	Hydrothermal carbonization	Mixing TW with $ZnCl_2$ at a ratio of 3:1 and urea at 5 wt.% of tea waste in deionized water, stirring continuously for 24 h under ambient temperature. Carbonization at 120–280 °C for 2 h, under 1.0–9.8 MPa pressure	Highest 80.7 at 120 °C	Guo et al. (2019)
Pruned tea waste	Biochar	Pyrolysis	Carbonization at 350 and 600 °C for 2 h, heating at a rate of 10 °C/min	–	Azeem et al. (2021)
Spent tea leaves after making tea infusion	Biochar	Pyrolysis	Carbonization of TW at temperatures of 300 and 700 °C for 2 h, with 7 °C min heating rate, followed by steam treatment for 45 min flowing at a rate of 5 mL/min	55.52 at 300 °C and 28.35 at 700 °C	Rajapaksha et al. (2014)
Tea pruning waste including leaves and stems	Biochar	Pyrolysis	Carbonization of the waste sample at various temperatures in the range of 250–500 °C for	Highest 61.46 and lowest 51.81 at 250 °C and	Borgohain et al. (2020)

(continued)

Table 11.1 (continued)

Precursor/ starting material	Porous carbonaceous product	Method of synthesis	Experimental conditions	Yield of adsorbent material (%)	References
			3 h with 25 °C/min heating rate	500 °C, respectively	
Waste tea branches	Biochar	Hydrothermal carbonization	Waste tea, KOH, and NH_4Cl solution were mixed at 3:1:1 ratio and immersed in deionized water for 24 h under constant stirring. Carbonization was done at temperatures 120–280 °C for 2 h, under 0.4–6.5 MPa pressure	Highest 80.9 at 120 °C	Guo et al. (2020a)

The hydrothermal method, however, gives a higher yield of biochar than pyrolysis. Further, HTC provides the biochar surface with many unique functional groups, while the high temperature of pyrolysis doesn't favor the development of many functional groups. The porosity of biochar produced by HTC method largely depends on the temperature, for instance, limited pores are formed in the biochar synthesized at 120 °C, whereas biochar prepared at 200 or 240 °C temperature have more meso and micro-pores on their surface. Pyrolysis is advantageous with respect to rapid conversion time and enlargement of surface area, but it has certain limitations like high temperature, high energy cost, and lower functional groups on the surface of the synthesized biochar. Hydrothermal method offers the advantages of low temperature, ease in processing, and plenty of functional groups on biochar surface (Guo et al. 2021). A combined method involving hydrothermal carbonization and pyrolysis together with $KHCO_3$ activation can remarkably increase the surface area of TW biochar (up to ~280-fold) and its pollutant (tetracycline) adsorption capacity (by around 40 times), as compared to one-step conversion (Li et al. 2021a). Nowadays, magnetic biochars are largely applied for adsorption purpose because of the ease in their post-adsorption separation, only by creating an external magnetic field. Magnetic biochar can be synthesized using TW by the steps of simultaneous carbonization, activation (using $KHCO_3$), and magnetization with $FeCl_3$. Magnetization together with chemical activation significantly enhances the mesoporous structure, total pore volume, and surface area of the synthesized biochar, resulting in higher (up to 14-fold) adsorption efficiency (Li et al. 2021b). As microwave heating can increase the speed of a reaction at even low temperatures, microwave assisted pyrolysis can be an energy-efficient and time-saving process for biochar production from tea waste with promising adsorption properties (Shirvanimoghaddam et al. 2021).

11.3.2 Wastewater Treatment by Tea Waste-Derived Adsorbents

Raw as well as modified tea waste and the various TW-derived porous carbonaceous materials such as activated carbon, biochar, etc. show excellent efficiency for the treatment of wastewater. The adsorption characteristics of such adsorbents and the potential towards the removal of different pollutants from aqueous medium are shown in Table 11.2. From the table, it is apparent that tea waste can effectively remove dyes, heavy metals, pharmaceuticals, toxic organic pollutants, etc.

11.3.2.1 Removal of Dyes

The effluents of textile industries impose serious concerns to aquatic environment because of the presence of high levels of hazardous organic dyes, dark color and components with poor biodegradability. It was already discussed that chemically modified TW shows excellent potential in dye adsorption. Likewise, tea waste-derived activated carbon and biochar are also highly efficient in the removal of a wide variety of cationic and anionic dyes, for example, methylene blue (Tuli et al. 2020), indigo carmine (Sikdar et al. 2020), malachite green (Akar et al. 2013), acid yellow 36 (Wijetunga and Gunasekara 2017), acid blue 29 (Auta and Hameed 2011a), acid blue 25 (Auta and Hameed 2011b), etc. Chemical modification significantly increases the dye removal efficiency of TW biochar. For instance, biochar prepared from phosphoric acid treated spent tea leaves showed excellent removal efficiency of around 99.3% for MB. Treatment with H_3PO_4 introduces various types of oxygen-containing functional groups on biochar surface which enhances the physio-chemical properties as well as adsorption characteristics of the biochar (Salehi et al. 2020). Similarly, modification using NaOH also improves the adsorption performance of TW-derived biochar by enhancing its mesoporous structure and active functional groups on the surface. These enhanced biochar properties attribute towards significant increase in dye adsorption through the mechanisms of hydrogen bond, pore filling, electrostatic attraction of the functional groups present in the molecules of dye with the biochar –COOH group, and π-π interaction with the biochar C=C group. As a result, 10 wt.% NaOH treated TW biochar displayed superb adsorption capacities of 105.3 mg/g for the cationic dye MB and 91.7 mg/g for the anionic dye orange-II (OR-II), while the dye uptake capacities were much lower in case of untreated TW, 69.27 and 54.80 mg/g for MB and OR-II, respectively (Mu and Ma 2021). Tea waste-derived ACs exhibited outstanding removal of 98–99% for MB, acid blue 25, and acid blue 29 (Auta and Hameed 2011a; Auta and Hameed 2011b; Tuli et al. 2020). The removal of other dyes like malachite green and cibacron yellow was also nearly 95% (Auta 2012; Akar et al. 2013). During the preparation of AC, the activating chemicals disintegrate the cellulose and lignin structure of TW, thus results in the formation of porous structure suitable for adsorption. The ACs usually have positively charged surface at lower pH that favors

Table 11.2 Adsorption of various types of contaminants from wastewater by waste-based adsorbents

Adsorbent	Feedstock	Specific surface (m^2/g)	Total volume of pores (cm^3/g)	Name of the pollutant	Percentage removal of pollutants (%)	Maximum pollutant adsorption capacity (mg/g)	References
Activated carbon	Domestic waste tea leaves	850.58	0.675	Methylene blue	98	238.10	Tuli et al. (2020)
Activated carbon (HNO_3 modification)	Factory tea waste	524	0.286	Methylene blue	96.54	683.60	Gokce and Aktas (2014)
Biochar (H_3PO_4 treatment)	Spent tea leaves	3.60	0.0093	Methylene blue	99.26	91.13	Salehi et al. (2020)
Biochar	Waste tea	–	–	Chromium (VI)	99.30	197.50	Khalil et al. (2020)
Biochar (modification using H_2SO_4, $NaNO_3$, $KMnO_4$, H_2O_2)	Domestic tea waste	11.83	0.0159	Fluoride	98.31	52.50	Roy et al. (2018)
Activated carbon	Factory tea wastes	45.50	0.136	Chromium (III)	95–100	61.00	Duran et al. (2011)
Activated carbon	Domestic tea residue	785	0.629	Oxytetracycline	–	273.70	Kan et al. (2017)
Biochar	Spent oolong tea waste	503	0.250	Chlortetracycline	97.40	627.00	Chen et al. (2022)
Porous gel	Factory tea waste	–	–	Chromium (III), lead (II), iron (III)	–	206.19, 253.16, 94.88, respectively	Zhang et al. (2020)
Iron nanoparticles	Green tea waste	42	0.0011	Phenol	94.80	–	Kadhum et al. (2021)

the sorption of anionic dyes, while the negatively charged surface of AC at high pH facilitates cationic dyes adsorption by electrostatic interaction (Garba et al. 2015; Tuli et al. 2020). A remarkable MB adsorption capacity of 683.60 mg/g was achieved with waste tea-derived AC treated with nitric acid. HNO_3 modification significantly increased the formation of acidic functional groups, mainly carboxylic groups on the AC surface which effected the removal of the basic dye MB through electrostatic forces (Gokce and Aktas 2014).

11.3.2.2 Removal of Heavy Metals

Several heavy metals can be successfully removed from wastewater using tea waste-based ACs and biochar, including trivalent chromium (Duran et al. 2011), hexavalent chromium (Khalil et al. 2020), nickel, cobalt (Shirvanimoghaddam et al. 2021), cadmium (Fan and Zhang 2021), and so on. AC synthesized from factory TW using H_2SO_4 activation can remove 95–100% of Cr(III) from real water samples such as tap water, stream water, and sea water (Duran et al. 2011). TW-based AC can also be used as electrode in capacitive deionization (CDI), for simultaneous Cr(VI) and fluoride (F^-) removal. When a mixed solution of chromium and fluoride with concentration 100 mg/L was fed into a CDI unit with TW-derived electrode, the maximum electro-sorption capacities for Cr(VI) and F^- were observed to be 2.8 and 2.5 mg/g, respectively. The higher removal of Cr (VI) may be attributed to the greater electro-sorption selectivity of divalent CrO_4^{2-} ion than the monovalent F^- ion (Gaikwad and Balomajumder 2017). A porous hydrogel adsorbent synthesized using waste tea residues showed outstanding adsorption capacities higher than 200 mg/g for Cr(III) and Pb(II). The adsorption of the heavy metals onto the TW-derived gel are found to be heterogeneous chemisorption, and in both the cases N and O-containing functional groups play the dominant roles in adsorption (Zhang et al. 2020).

Biochar prepared by pyrolysis of waste tea exhibited over 99% removal efficiency and a high adsorption capacity of 197.5 mg/g for hexavalent chromium. The adsorption of Cr(VI) onto TW biochar is well explained by pseudo-second-order kinetic model indicating chemisorption, and Langmuir isotherm is best fitted to the equilibrium of the adsorption process representing monolayer sorption. Different functional groups present on the surface of TW biochar like –OH, COO–, and $–NH_2$ were associated with Cr(VI) adsorption through the mechanism of ion exchange (Khalil et al. 2020).

A TW-derived magnetic biochar presented excellent adsorption capacities of 160.00 mg/g and 131.68 mg/g for the heavy metals nickel (Ni^{2+}) and cobalt (Co^{2+}), respectively. Figure 11.4 depicts the schematic flowchart for the synthesis of magnetic TW biochar and its application for heavy metal removal. Domestic TW was initially washed with deionized water, oven-dried at 250 °C for 3 h, and then the magnetic biochar was prepared using three different approaches: (1) heat-treated TW was first carbonized and magnetized using ammonium iron(II) sulfate, both the operations in two tube furnaces in presence of nitrogen atmosphere, (2) initially

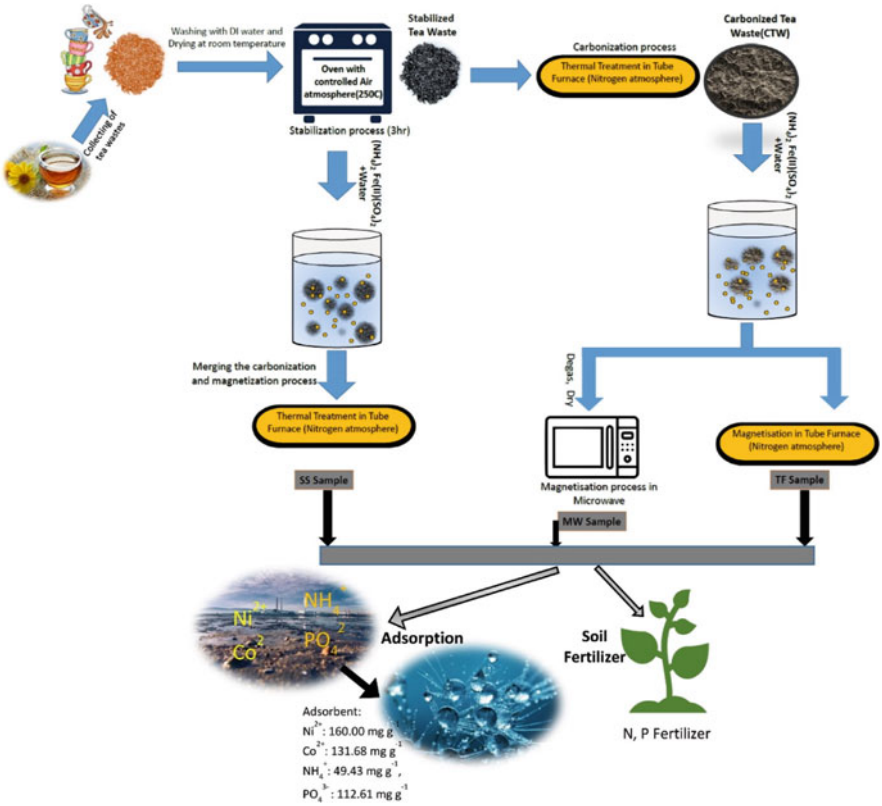

Fig. 11.4 Magnetic biochar production using tea waste and its application for the adsorption of heavy metals. (From Shirvanimoghaddam et al. (2021))

the heat-treated TW was carbonized in a tube furnace and then magnetized in a microwave oven for 10 s, and (3) single-stage process, in which both carbonization and magnetization were performed together in the same tube furnace in presence of N_2. The magnetization process introduces magnetic iron oxide (Fe_3O_4) nanoparticles on the biochar surface homogenously and develops a porous structure in the TW biochar. The adsorption of Ni^{2+} and Co^{2+} by the TW-derived biochar occurred through chemisorption. The biochar was also able to adsorb nutrients released from the fertilizer's activity like NH_4^+ (ammonium) and PO_4^{3-} (phosphate), with maximum sorption capacities of 49.43 and 112.61 mg/g, respectively. Hence, magnetic TW biochar can be utilized in wastewater treatment to remove heavy metals and also for slow fertilizer release to improve the composition of soil (Shirvanimoghaddam et al. 2021). Tea waste biochar prepared at three different pyrolysis temperatures of 200, 500, and 700 °C showed maximum cadmium adsorption capacities of 8.90, 4.73, and 7.26 mg/g, respectively. The functional groups of TW waste biochar interact with Cd ions through different mechanisms including surface complexation, ion exchange, precipitation, and cation-π interaction. The

oxygen-containing functional groups are dominant in surface complexation in low temperature biochar, while the aromatic structure is involved in Cd removal by the high temperature biochar (Fan and Zhang 2021).

11.3.2.3 Removal of Pharmaceutical and Other Contaminants

Pharmaceuticals are a group of emerging pollutants released from hospitals, industrial activities, municipal sewage, and wastewater treatment plants effluents. Tea waste and its derivative adsorptive materials are widely utilized in the treatment of pharmaceutical-contaminated wastewater. A number of pharmaceutical pollutants can be removed effectively from the aquatic environment using TW-based adsorbents such as tetracycline, chlortetracycline, oxytetracycline, sulfamethazine, sulfadiazine, acetaminophen, sodium diclofenac, and so on (Debnath et al. 2020, 2022). Domestic TW-derived AC prepared under steam revealed high potential for the removal of oxytetracycline (OTC), the maximum adsorption capacity being as high as 273.7 mg/g. The dominant mechanism behind the adsorption is ion exchange. The OTC^+ cations get adsorbed onto the AC surface by substituting the H^+ ions present on the surface hydroxyl (-OH) groups (Kan et al. 2017). AC prepared from spent TW using H_3PO_4 activation shows the ability to remove 94.3% of the pharmaceutical aspirin, while the maximum aspirin uptake capacity is observed as 178.6 mg/g which is greater than most of the available adsorbents of aspirin. H_3PO_4 activation of the spent TW resulted in outstanding surface properties (51% porosity and an enlarged surface area 1200 m^2/g), which is attributed to the excellent aspirin adsorption (Wong et al. 2018a). Similarly, spent tea leaves-derived AC (H_3PO_4 activation) exhibited a superb removal efficiency of 99.87% for another pharmaceutical pollutant acetaminophen. Treatment with H_3PO_4 disintegrates the hemicellulose present in the waste tea leaves into monosaccharides and also breaks the chemical bonds in lignin, thus forming a porous structure. Besides, some volatile compounds (H_2O, CO_2, CO, and CH_4) are generated due to the reaction between the spent tea waste and acid, the release of which further enhances the pore network and thereby the adsorption behavior of AC gets improved (Wong et al. 2018b).

Due to the presence extensive surface area and large pore volume, TW-derived biochar are also found as promising adsorbents for pharmaceutical removal. TW biochar can remove ~99% chlortetracycline (Chen et al. 2022) and 95–99% of tetracycline (Li et al. 2021a; Mu et al. 2021) from aqueous systems. An extraordinarily high adsorption capacity 627 mg/g could be achieved for chlortetracycline using spent oolong tea-derived biochar. Adsorption of chlortetracycline by TW biochar best fits to pseudo-first-order kinetic model indicating physical adsorption or diffusion, and the adsorption isotherm obeys the Freundlich model representing multilayer adsorption (Debnath et al. 2020). Biochar prepared from factory TW by a combined method involving $KHCO_3$ activation, hydrothermal treatment, and pyrolysis exhibits outstanding adsorption capacity more 450 mg/g for tetracycline. The mechanisms behind TC adsorption onto TW biochar involve pore filling, surface complexation, H-bonds, π-π interaction, and electrostatic attraction (Li et al. 2021a).

Apart from the above contaminants, tea waste can be utilized for the removal of several other pollutants such as arsenic, fluoride, polycyclic aromatic hydrocarbons (PAH), organic compounds (COD), phenol, and so on. A magnetic porous carbon material produced utilizing tea processing waste offered maximum arsenic adsorption capacity as 38.03 mg/g, which is notably higher than other arsenic adsorbents such as activated alumina (0.18 mg/g), iron oxide coated sand (0.041 mg/g), pine wood char (0.0012 mg/g), cobalt ferrite nanoparticles loaded schwertmannite (1.01 mg/g), etc. The adsorption process is dominated by ion exchange mechanism between As(V) and the -OH groups on the TW-derived adsorbent surface (Dey et al. 2014; Wen et al. 2017). TW biochar subsequently modified with sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), and hydrogen peroxide (H_2O_2) showed a remarkable maximum fluoride removal efficiency of 98.3%. De-fluoridation by TW biochar is a spontaneous, endothermic, and physicochemical adsorption. The maximum F^- sorption ability of 52.5 mg/g could be achieved employing the chemically reduced TW-based biochar that is greater than many other F^- adsorbents. Chemical treatment on the TW biochar increases the size and total volume of pores, while enhancing the surface area as substantial quantities of oxidizing agents are present in the modified biochar, and these surface properties are ascribed to its improved adsorption ability (Roy et al. 2018). Magnetic nanocomposite can be produced using green TW-derived AC to adsorb different PAHs such as benzo[*a*]anthracene, chrysene, benzo[*a*]pyrene, and benzo[*b*] fluoranthene from aqueous medium. The TW-based nanocomposite exhibited a very fast adsorption rate, removing 80% of the pollutants within 5 min of contact. The adsorbent could be recycled up to 5 times with no significant loss of removal capacity. It has the capability to remove 72–89% of these PAHs from mineral water having PAH concentration of 1 mg/L, and in case of tap and river water the removal efficiency is almost 100% (Inbaraj et al. 2021).

11.3.3 Purification of Drinking Water

Like wastewater treatment, waste tea can also be utilized for the purification of drinking water as well. Iron/aluminum oxides loaded TW can efficiently remove fluoride from contaminated drinking water. The TW-based composite revealed a greater fluoride adsorption capacity of 18.5 mg/g as compared to raw TW that shows a capacity of 3.8 mg/g. Using this adsorbent, the F^- level in drinking water was brought down below 1.5 mg/L, which is the standard drinking water fluoride concentration as specified by World Health Organization (WHO). The post-adsorption residual iron and aluminum levels in the treated water also met the WHO limits. The fluoride adsorption efficiency of the TW composite is better than many of its bio-based adsorbents such as wheat straw, chitosan, zirconium loaded cellulose, aluminum oxide incorporated charcoal, cashew nut shell, etc. (Cai et al. 2015). Factory tea waste, modified using zirconium (Zr) by extrusion technique, has the ability to remove 97% F^-, which is significantly higher than the unextruded

TW-Zr composite that shows an efficiency of 61%. Due to extrusion, more functional groups are exposed and size of pores get increased which leads to enhanced adsorption capacity. Adsorption of fluoride by Zr-loaded TW best fits to pseudo-second-order kinetics suggesting chemisorption and Langmuir isotherm suitably described the adsorption equilibrium representing monolayer adsorption with maximum sorption ability as high as 20.6 mg/g (Mei et al. 2019). Apart from defluorination, TW is also useful for eliminating turbidity and TDS from drinking water. AC derived from waste tea bags as well as open TW exhibits promising potential to decrease the TDS value of canal water from 260 mg/L to 23–24 mg/L and the TDS of lake water from 420 mg/L up to 41–49 mg/L. Canal water had a turbidity of 90 NTU that could be reduced to 3.01 NTU, while lake water turbidity of 24.63 NTU reached to 3.69 NTU, using the TW-based AC. Furthermore, the AC increased the DO (dissolved oxygen) of canal water from 4.9 to 7.9 mg/L and lake water DO from 4.9 up to 7.0 mg/L. This substantial improvement in DO levels shows the effectiveness of TW-based ACs in purifying the water of lake as well as canal (Tahir and Choudhry 2017). TW biochar can effectively remove a toxic pesticide carbofuran from drinking water (adsorption capacity 10.2 mg/g). Carbofuran adsorption by TW biochar may follow different mechanisms including physisorption through H-bonds, π^{+}–π interactions, Van der Waals attraction, and also chemisorption via chemical bonding among the amine group of carbofuran and phenolic group of TW biochar (Vithanage et al. 2016).

11.3.4 Remediation of Air and Soil

Recently, tea waste is being utilized in the remediation of other elements of the environment also such as air and soil. Tea waste powder has been found to be very effective for carbon dioxide removal from air. TW powder treated with microwave exhibited CO_2 adsorption capacity of 0.00892 mmol/g, whereas untreated TW showed 0.00267 mmol/g capacity under a column pressure of 3 kg/cm^2. The adsorption capacities shown by TW adsorbents for CO_2 are more than commercial carbon that has 0.000781 mmol/g adsorption capacity at 3 kg/cm^2. Treatment with microwave considerably enhances the TW powder surface area and increases the carbon content, thus resulting in improved adsorption performance (Dhage and Kulkarni 2015). TW-derived AC modified with ethylenediamine can efficiently remove CO_2 from biogas. Pristine and modified TW-based ACs show adsorption capacities of 87.42 and 108.97 mg/g, respectively, for pure CO_2. When applied to swine farm biogas containing 40% CO_2, adsorption capacities of 60.64 and 78.98 mg/g could be reached, respectively (Rattanaphan et al. 2020). Magnetic TW biochar can effectively remove mercury (Hg) from coal syngas with nearly 96% efficiency and the biochar delivered more than 90% removal even after 6 cycles of application (Altaf et al. 2021).

In soil, immobilization or abetment of heavy metals can be achieved by employing waste tea-derived biochar. A 10% dosage of TW biochar to

cadmium-contaminated sediment can cause 67.7% reduction in the exchangeable Cd fraction (Pal and Maiti 2019), which is greater than many other materials like coal gangue with 14.2–29.8% Cd reduction and corn stover/attapulgite composite that shows 32.1% Cd immobilization efficiency (Debnath et al. 2022). Green TW-based porous biochar supported iron material exhibited about 80% immobilization of Cd and PB, when used in heavy metal contaminated soil of an industrial area (Qian et al. 2022).

11.4 Application of Tea Wastes for the Generation of Bio-Energy

Tea waste has the potential to support the rapidly increasing global energy demand up to a great extent by generating bio-energy to be used as electricity, heat, and transportation fuels. TW is a naturally available, abundant, clean, renewable, and affordable source of bio-fuel that can successfully replace the traditional petroleum-derived fuels in the road transportation sector. The lignocellulosic TW biomass contains fermentable sugars which can be transformed into biofuel (Debnath et al. 2021b). The high calorific value of TW (17.23 MJ/kg) makes it a promising resource for the production of solid fuel pellets with desirable properties like 17.39 MJ/kg calorific value, 99.93% durability index, and 9.58% moisture content (Pua et al. 2020).

11.4.1 Gaseous Biofuel

Tea waste is generally used as a co-substrate with other waste materials in anaerobic digestion process to generate a renewable gaseous fuel, named biogas. Digestion of spent TW along with fresh cow manure in anaerobic reactor (at 37 ± 2 °C for 25 days, C/N = 24.96) offers a high biogas yield (0.82 mL/g VS), having high methane content around 70%, remarkable calorific value of 26.4 MJ/kg, and energy content of 5.1–5.7 kW/m^3 (Khayum et al. 2018). Co-digestion of 25% spent tea waste and 75% cow manure (at 37 °C for 20 days, inoculum/substrate ratio 2) can produce maximum bio-methane yield of 181 ± 7 mL/g VS (Gozde Ozbayram 2021).

The schematic representation of biomethane production using TW as a co-substrate is illustrated in Fig. 11.5. Mixing spent TW powder with carbon-rich organic wastes in anaerobic digestion process can increase the production of biomethane by four fold than that obtained from mono-digestion of the wastes. The abundant nitrogen contained in the TW powder is attributed to the remarkable enhancement in biomethane yield. When waste feedstocks are mixed at a ratio of 1: 2:1 (organic waste/TW powder/activated sludge) and subjected to anaerobic

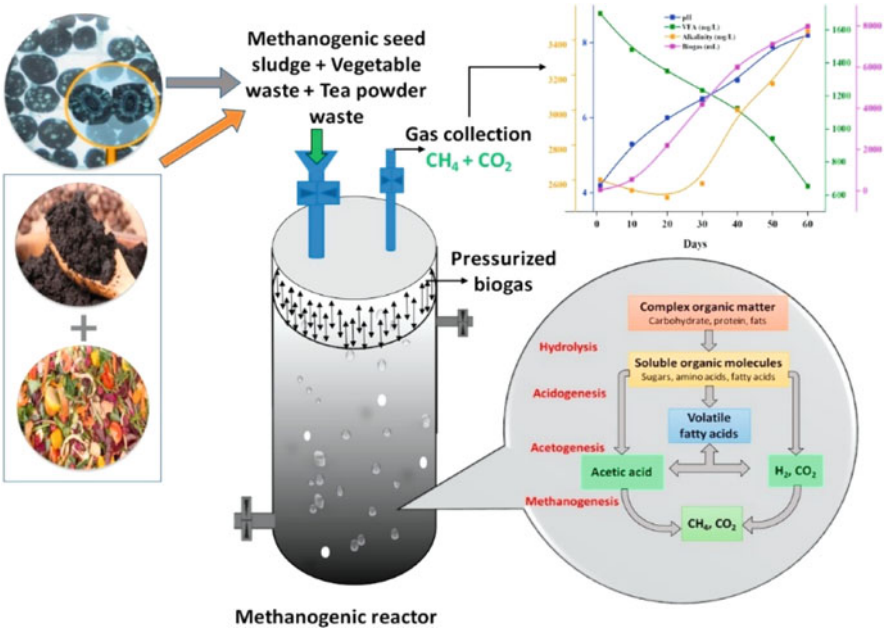

Fig. 11.5 Production of biogas by co-digestion of TW powder and organic wastes. (From Thanarasu et al. (2018))

digestion at 35 ± 2 °C, the methane production rate observed after 30 days is as high as 536 mL/d (Thanarasu et al. 2018).

11.4.2 Liquid Biofuel

Tea waste is also a suitable precursor for the production of liquid biofuel such as bio-oil and bioethanol to substitute the petroleum-derived transportation fuels. Pyrolysis of factory TW (at 500 °C with 40 °C/min heating rate) having a calorific value of 18.5 MJ/kg provides 26.80% yield of bio-oil with heating value as high as 29.11 MJ/kg (Basumatary et al. 2018). Waste tea is a carbon-rich material with substantial amounts of glucose, xylose, maltose, galactose, mannose arabinose, and other sugars. Fermentation of these reducing sugars using yeast can convert them into bioethanol with yield close to the theoretical value (Debnath et al. 2021b). Hydrolysis of spent TW with 8% H_2SO_4 and subsequent fermentation using *Saccharomyces cerevisiae* enzyme (1% inoculant) followed by distillation produced alcohol with bioethanol level of 8.2% (Afdhol et al. 2019). Fermentation of TW hydrolysate using three different yeast species, namely, *Scheffersomyces stipitis* (ATCC 58784 and ATCC 58785) and *Saccharomyces cerevisiae* resulted in

38.9%, 33.9%, and 35.9% yield of bioethanol, respectively, near to the theoretical ethanol yield (51.1%) obtained from glucose (Germec and Turhan 2018).

In biodiesel production, waste tea can be utilized as catalysts for esterification of fat/oil. Sulfonated black TW shows excellent catalytic activity in the esterification of palm fatty acid distillate. The TW catalyst could cause 97% conversion of the free fatty acids into biodiesel. Minimal requirement of temperature, cheap cost, and multiple recyclability (up to 5 times) make the TW-derived catalyst effective and feasible for bulk scale industrial production of biodiesel (Rashid et al. 2019). Biodiesel has a major disadvantage that limits its efficient usage. Aging due to oxidation adversely affects the biodiesel storage stability. Natural antioxidants extracted from green and black tea leaves are found to be effective in improving the oxidative stability of biodiesel. The American, Indian, and European standard specifications of induction period (IP) for biodiesel stability are 3 h, 6 h, and 6 h, respectively. It has been observed that alcoholic extracts of black and green can significantly increase the IP of biodiesel up to 9.2 h and 6.9 h, respectively (Correia et al. 2020). Antioxidant phenolic components inhibit the oxidation of biodiesel and thus enhance its stability. Since tea waste is also a rich source of antioxidant polyphenols like the regular tea leaves, it can be utilized as an environment-friendly, cheap, and emerging natural antioxidant to improve biodiesel stability during long-term storage (Debnath et al. 2021b).

11.5 Other Utilization of Tea Wastes

Apart from the applications discussed in the earlier sections, tea waste may be utilized in several other fields also. Some of the emerging applications of TW include electrode material in energy storage devices such as high performance supercapacitors (Ratnaji and Kennedy 2020) and batteries (Gao et al. 2021), preparation of biodegradable plastic (Liu et al. 2020), synthesis of valuable metal nanoparticles (Gautam et al. 2018), sustainable building materials production (Caronge et al. 2022), etc.

A hierarchical porous carbon material prepared from domestic spent TW (pre-carbonization at 400 °C for 4 h followed by impregnation with KOH at 50 °C for 18 h and activation at 800 °C for 2 h), when used as cathode in supercapacitor containing 1 M Na_2SO_4 (sodium sulfate) electrolyte, exhibited excellent electrochemical performance with 490 F/g capacitance and around 99.7% retentivity of the capacitance even after completing 1000 cycles at a current density of 8 A/g. The TW-based electrode had a large surface area (806 m^2/g) and high mesopore volume (0.075 cm^3/g), which are associated with its high capacitance. Diffusion and adsorption of electrolyte ions into internal micropores is facilitated by the mesopores, and they also prevent the ions from accumulating at the mouth of micropores, thus leading to enhanced charge accumulation improving the electrochemical characteristics of the electrode (Ratnaji and Kennedy 2020). Tea waste-derived porous carbon materials are also useful as the electrodes of potassium ion hybrid capacitors,

potassium ion batteries, lithium-ion batteries, lithium sulfur batteries, sodium ion batteries, etc. because of their promising electrochemical properties (Debnath et al. 2021b). When spent black tea-derived carbon anode is used in potassium ion batteries, it can provide a highly reversible capacity of 491.6 mAh/g at 50 mA/g current density, with long-term durability by retaining 102.1 mAh/g capacity at current density of 1 A/g even after completing 2300 cycles. The TW-based anode revealed ultra-long-term cycling stability in potassium ion hybrid capacitors, with capacity as high as 54.2 mAh/g even after completion of 10,000 cycles at current density 3 A/g. The highly porous network of spent TW-derived carbon enables fast transfer of ions and electrons, thereby improving the storage stability (Gao et al. 2021).

Since tea waste is a cellulose-rich material, another potential utilization of this waste biomass may be the synthesis of valuable crystalline derivatives of cellulose like microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC). With the help of an appropriate pretreatment, the rigid lignin layer in can be broken for the separation and subsequent utilization of the individual components such as cellulose, hemicellulose, and lignin. Both MCC and NCC are highly valuable cellulosic derivatives that are immensely applicable in the environmental sector, polymer composites, and also in biomedical as well as pharmaceutical fields (Debnath et al. 2021a, b). Acid hydrolysis (1.5 M HCl at 65 °C for 90 min) of waste oolong tea can yield 86.70% MCC. The TW-derived MCC possess good thermal stability and other desirable properties for use in bio-composites. NCC was also isolated from agricultural waste tea-stalks through acid hydrolysis using H_2SO_4, with a yield of 49.87%. The thermal stability of TW-derived NCC has been found to be better than that of the NCCs isolated from commercial MCC or wood biomass (Zhao et al. 2018; Guo et al. 2020b).

In the present era, green synthesis of nanoparticles (NPs) employing bio-based materials has gained increasing interest from the view point of environment and sustainable development concerns. In this regard, tea waste shows promising potential towards the synthesis of different metal nanoparticles such as silver (Ag) NPs, iron (Fe) NPs, as well as metal oxide (iron oxide) nanoparticles. The polyphenolic components (mainly catechin) of TW plays a vital role in nanoparticle synthesis by reducing the metal salts and also acting as capping as well as stabilizing agents for the formed NPs. The polyphenols' structural features induce delocalization of electrons, thus showing high activity in free radical quenching. Utilization of TW for nanoparticle synthesis can be an effective, environment-benign, and low-cost method, without the use of toxic chemicals or generation of hazardous by-products (Debnath et al. 2021b).

Biodegradable plastic films can be fabricated using tea waste to be used as sustainable packaging material. Bioplastic synthesized by employing tea industry waste and citric acid plasticizer show strong hydrophobic properties with water contact angle up to 117°, acceptable mechanical properties such as 6.16 MPa ultimate tensile strength and 13.33% elongation at break. Moreover, the TW-based plastic has been observed to decompose easily in the environment through aerobic microbial activities. Preparation of bioplastic from TW is a facile and green method

that is completely non-toxic with zero waste production, requiring mild conditions and also less processing time. Such TW-derived hydrophobic bioplastic can replace the conventional petroleum-derived plastic materials in the packaging sector, thereby minimizing the excessive usage of petroleum resources to prevent their depletion and at the same time reduce the environmental pollution load caused by those non-biodegradable plastic packaging (Liu et al. 2020).

Utilization of tea waste as a natural fiber for the production of green concrete has been explored recently. The building construction sector is one of the key contributors to global greenhouse gas emission, particularly CO_2. Construction of a building generate CO_2 both directly and indirectly, around 14% directly from combustion of natural gas, diesel, light fuel oil, and about 85% indirectly from the consumption of electricity. Among the different construction materials, concrete is the most carbon-emitting which accounts for somewhere in between 60 and 70% of the total embodied carbon. Concrete industry is responsible for around 10% of the worldwide industrial CO_2 emissions, which is mainly caused by the production of Portland cement. Around 0.9 ton of CO_2 is generated for the production of 1 ton of Portland cement. Therefore, using tea waste ash as a supplementary cementitious material in concrete can be an alternative way to reduce the emission of CO_2 up to a great extent. In view of that, a sustainable green concrete was produced by replacing cement with an agricultural industrial waste, i.e., processed tea waste ash, which is generated after burning the solid tea processing wastes as a boiler fuel. It has been observed that concrete with 10% (by weight) processed TW ash as cement replacement possesses similar compressive strength as control concrete (made up with 100% cement) after 28 days of curing, and in case of longer curing period of 90 days, the strength of the TW embedded concrete is around 4.57% higher than the control concrete. This increase in strength at the later age of concrete is ascribed to the continuous pozzolanic reaction of TW ash. Furthermore, the incorporation of 10% processed TW ash could significantly decrease the intensity of embodied carbon and CO_2, amounted to 8.32 and 7.85%, respectively, in comparison with pristine cement concrete. So, it is apparent that waste tea may be utilized as an innovative building material for partial substitution of Portland cement, with respect to environment-friendly and sustainable development (Caronge et al. 2022).

Likewise, tea waste can be used as pore making additives in the production of clay bricks to decrease the excessive consumption of clay resources and also the lightness of the brick body. Porosity of bricks prepared with various levels of domestic spent tea leaves (2.5, 5, 7.5, 10, and 12.5%, by weight) lied in the range of 30.1–48.8%. Brick porosity tends to increase with the rise in tea waste concentration, and 12.5% TW can increase the porosity up to 56.5% as compared to neat clay fired bricks. However, increment in TW concentration reduced the compressive strengths of the baked bricks. Compressive strength is a very crucial parameter with respect to structural applications of construction materials. The minimum compressive strength of building materials must be 7 MPa as per the European and Turkish Standards. Brick containing 12.5% TW possesses compressive strength of 6.9 MPa, whereas a brick with 10% TW having compressive strength more than 10 MPa meets

the standard of strength. Hence, the addition of TW up to 10% in clay fired brick is feasible for building applications (Ozturk et al. 2019).

11.6 Conclusions

Tea is a highly popular beverage with extensive worldwide consumption due to its superb health promoting activities. Tea consumption is increasing remarkably all over the world, and as a consequence the generation of tea wastes is also increasing substantially. The tea industries around the world produce enormous amounts of wastes as the by-products of tea processing. In addition to that, the spent tea leaves discarded after infusion further increase the waste load on the environment. These huge quantities of waste tea are generally disposed by dumping or burning, which causes a number of environmental issues.

Tea waste shows excellent potential towards a wide variety of applications. The waste tea leaves contain abundant amounts of bioactive polyphenolic compounds, which make them a promising source for the extraction of antioxidants like catechin. Other pharmaceuticals such as flavonoids and caffeine may also be extracted from waste tea residues. Waste tea, both in pristine and modified forms, shows outstanding performance as adsorbents for the removal of dyes, heavy metals, organic, and pharmaceutical pollutants from the water environment. The rich carbon content of TW makes it a suitable precursor for the production of some carbon-rich high efficiency adsorbents like activated carbon and biochar. A large number of pollutants including chromium, lead, nickel, arsenic, methylene blue, EBT, congo red, tetracycline, aspirin, chlortetracycline, oxytetracycline, etc. can be removed efficiently (over 90% removal) from wastewater using the adsorbents synthesized from tea waste. Recently, TW-derived adsorptive materials are also utilized in the treatment of drinking water for defluorination and turbidity or TDS removal. Further, air and soil clean up may also be accomplished using waste tea. Different forms of bio-energy such as biogas, bio-methane, bio-diesel, and bio-ethanol can be generated using waste tea leaves. TW-derived porous materials exhibit outstanding electrochemical performance when used as electrodes in energy storage devices like supercapacitors or batteries. Moreover, TW can be utilized for the preparation of sustainable building materials (bricks, concrete), biodegradable plastic packaging, value-added cellulosic derivatives, metallic nanoparticles, and so on. However, the real-life applications of TW are not yet flourished. Development of modern technologies with the help of further scientific investigations will assist in the potential utilization of TW in different fields to promote the “waste to wealth” strategy.

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Part III
Bioactive Metabolites from Agricultural Waste

Chapter 12
Vitis Wastes as a Source of Stilbenes: Natural Occurrence, Factors Affecting Biosynthesis, and Valorization in Agri-Food Sector

Julien Gabaston, David Taillis, and Emma Cantos-Villar

Abstract The *Vitis* grapevine is a plant grown worldwide which is used to produce wine, juice, table grapes, or dried grape berries. A key step in obtaining good-quality fruit is a suitable management of the vineyard. Pruning, vineyard removal, leaf trimming, and destemming are vitivinicultural practices that generate a huge amount of waste in the form of canes, stems, leaves, trunk, and roots. Generally discarded, burned in the open air, or left on vineyard soil, the several millions of tons of *Vitis* wastes produced each year could be incorporated into a recycling model that promotes a shift from a linear to a circular economy. Grapevine biomass is enriched in stilbenes, plant phytoalexins known for their human health benefits, and represents an interesting biomass to evaluate. The aim of this chapter is to decipher the stilbene composition in the different kinds of grapevine waste, especially canes, stems, leaves, trunk, and roots. An analysis was performed of the various factors which could modulate biosynthesis of stilbenes in each grapevine waste, such as genetic, biotic, abiotic, and human factors. Finally, the chapter highlights the different bioactivities of *Vitis* waste and their potential applications in agriculture, medicine, pharmacy, cosmetics, oenology, and the food industry.

Keywords *Vitis* canes · *Vitis* stems · *Vitis* leaves · *Vitis* trunk · *Vitis* roots · Stilbenes · *Vitis*

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Abbreviations

Aβ	Beta-amyloid peptide
ABTS	2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)
AChE	Acetylcholinesterase
DNA	Deoxyribonucleic acid
DPPH	2,2-Diphenyl-1-picryl-hydrazyl-hydrate
DW	Dry weight
EU	European Union
FW	Fresh weight
GAE	Gallic acid equivalent
HRMS	High resolution mass spectrometry
IC_{50}	Concentration of a product inhibiting 50% of the observed effect
iNOS	Inducible nitric oxide synthase
MeJA	Methyl jasmonate
MIC	Minimal inhibitory concentration
MS	Mass spectrometry
ND	Not detected
NQ	Not quantifiable
Nrf2	Nuclear factor erythroid 2-related factor-2
ORAC	Oxygen radical absorbance capacity
PAL	Phenylalanine ammonia lyase
PR	Pathogenesis-related
RGM	Riparia Gloire de Montpellier
ROS	Reactive oxygen species
RSB1	Rességuier Selection Birolleau 1
Ru	Ruggeri 33
SIRT	Sirtuin-activating
SO_2	Sulfur dioxide
SO4	Selection Oppenheim 4
STS	Stilbene synthase
U-HPLC	Ultra high performance liquid chromatography
UV	Ultra-violet
VEGF	Vascular endothelial growth factor

12.1 Introduction

Vitis vinifera, commonly known as grapevine, is a perennial woody plant grown in many parts of the world for the production of grape berries. A total of 7,400,000 hectares (ha) are dedicated to the cultivation of this fruit in the world, almost half of these in the European Union (3,200,000 ha) (International Organisation of Vine and Wine Intergovernmental Organisation 2019; Aliaño-González et al. 2020). Mainly

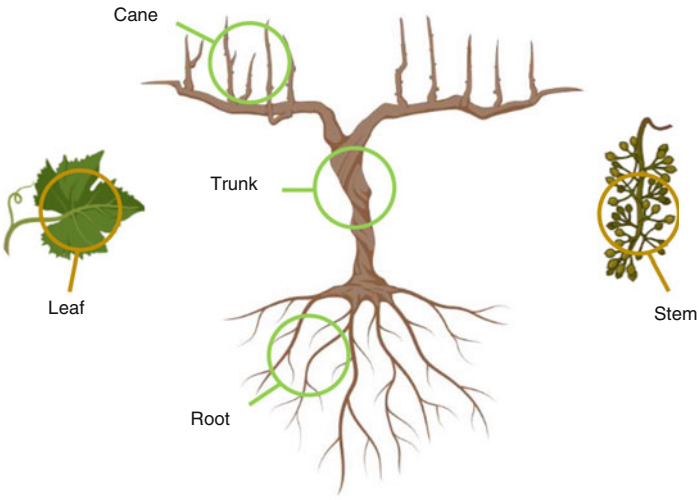


Fig. 12.1 Wastes from grapevine: cane, trunk, root, leaf, and stem

produced by Spain, Italy, France, and China, the world production reached 77.8 million tons of berries in 2019, 57% of which are used for wine production, while other uses include table grape consumption (36%) and dried fruit production (7%) (International Organisation of Vine and Wine Intergovernmental Organisation 2019).

As the quality of the fruit largely depends on good vineyard management, viticultural practices generate a huge amount of grapevine wastes every year. Firstly, at the end of summer, a month before the fruits ripen, leaf trimming takes place. This involves removing all the leaves hiding the clusters from the sun, which leads to a huge amount of biomass (Fig. 12.1) (Baroi et al. 2022). Later, during the winter season, grapevine pruning is an important process consisting of cutting hardened/woody shoots, known as grapevine cane. The aim of this is to reduce the number of bunch stems, thereby allowing a better distribution of nutrients and an effective light exposure of the canopy (Fig. 12.1) (Velázquez-Martí et al. 2014). An estimated volume of between 2 and 5 tons per hectare per year is obtained, leading to more than 15 million tons of canes worldwide (Guerrero et al. 2016). Likewise, driven by factors such as agricultural practices (aged vineyard, modernization or reconversion of plantations), food markets (grape variety changes or other fruit development), or others (plague/disease), the entire vineyard could be removed, thus generating a significant amount of grapevine wood/trunk and roots (Fig. 12.1) (Aliaño-González et al. 2020). Generally, vineyards produce each year 79% of waste canes and 21% of waste trunk and roots (Gabaston et al. 2017). Overall, it has been estimated that discarded trunks and roots create a biomass weighing 4 million tons each year. Grapevine cluster stems (also known as bunch stems) are another ligneous waste from vitivinicultural practices that is accumulated during the destemming process (Fig. 12.1). Destemming entails removing grape berries from the stems, an essential procedure since cluster stems introduce undesirable green tannins and herbaceous

and vegetable aromas to the wine (Bavaresco et al. 1997). Commonly, these lignified side-streams represent from 3 to 6% of the raw matter processed in a winery, i.e., 60 kg/tons of raw matter (Spatafora et al. 2013). All these *Vitis* wastes are mostly under-utilized, and are generally discarded, burned in the open air or dropped onto the ground. However, they are enriched in high added-value compounds and could be reused and exploited in multiple areas as valuable products.

This model of valorization is part of the circular economy model, which consists of turning waste into an efficient resource, therefore extending the life cycle of products. The linear economy is predominant in industry, where raw materials are collected, and then transformed into products that are used until they are finally discarded as waste. Currently, the EU encourages and challenges companies to move from a linear to a circular economy, closing the loop, and it proposes that biomass wastes be repeatedly valorized Circular Economy: Definition, Importance and Benefits (n.d.).

In order to value grapevine wastes, scientific research relies on their high stilbene content. Stilbenes are phenolic compounds possessing a C6-C2-C6 structure which derive from the secondary plant metabolism. From monomers to octamers, the stilbene family consist of a wide range of compounds with various derived forms such as glycosylated, methylated, isomerized, and isoprenylated functions (Pawlus et al. 2013; Lambert et al. 2013). Stilbenes are particularly known to act as phytoalexins and to be produced by the plant during pathogen attack to defend itself (Schnee et al. 2013). Stilbenes have also attracted great interest in the scientific community due to their benefits for human health such as chemopreventive, neuroprotective, and cardioprotective activities (Saiko et al. 2008; Richard et al. 2011; Ko et al. 2017). They are widely present in the vegetative parts of the grapevine such as the canes, stems, leaves, wood, and roots (Mattivi et al. 2011; Gabaston et al. 2019). The average stilbene content in the whole plant is in the range of grams per kilogram, i.e., about 1000-fold more than in berries (Lambert et al. 2013). Being rich in stilbenes, *Vitis* wastes represent an interesting and sustainable biomass to value in order to move toward a circular economy.

This chapter describes the stilbene composition of *Vitis* wastes (canes, stems, leaves, wood, and roots) as well as the different factors influencing their biosynthesis. We investigate the recent advances in the valorization of grapevine biomass in the agri-food industry, as in agricultural, medicinal, pharmaceutical, cosmetics, oenological, and food areas with the goal of considering potential recovery of these vitivinicultural wastes.

12.2 Vine Wastes: Canes

12.2.1 Stilbene Composition in Grapevine Canes

Over the past 15 years, grapevine canes have attracted great interest in scientific domains owing to their great availability and richness in stilbenes. More than

30 stilbenes have been well-described in the cultivated *V. vinifera sativa* used for wine production (Lambert et al. 2013; Ferreyra et al. 2020; Escobar-Avello et al. 2021a; Noviello et al. 2022) or table grape production (Guerrero et al. 2016) as well as in the ancestral *Vitis vinifera sylvestris* vine (Guerrero et al. 2016) or the American and Asian wild *Vitis* species (Pawlus et al. 2013; Loupit et al. 2020). Monomers (*E*- and *Z*-piceid, *E*-piceatannol, *E*-resveratrol, *E*-resveratroloside, *E*-and *Z*-astringin), dimers (ampelopsin A, ampelopsin F, pallidol, *E*-parthenocissin A, *E*-ε-viniferin, *E*-ω-viniferin, E-δ-viniferin, vitisinol C, scirpusin A, restrytisol, caraphenol), trimers (*E*-miyabenol C, *E*-ampelopsin E, *E*-amurensin B, α-viniferin), and tetramers (viniferol E, hopeaphenol, isohopeaphenol, ampelopsin H, r2-viniferin, r-viniferin, vitisin C) have been characterized in canes (Pawlus et al. 2013; Lambert et al. 2013; Gabaston et al. 2019; Guerrero et al. 2020) (Table 12.1). Uncommon stilbenes such as the hexamer viniphenol A have also structurally elucidated in *V. vinifera* cane on the basis of spectroscopic data analysis and molecular modeling under nuclear magnetic resonance constraints (Papastamoulis et al. 2014).

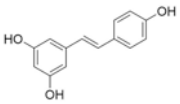
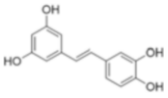
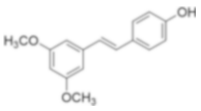
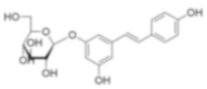
Regarding the quantity of stilbenes in grapevine canes, several authors have compared the different *V. vinifera* cultivars used for wine production. Lambert et al. (2013) showed that the most abundant stilbenoid was the dimer *E*-ε-viniferin (mean of 2.2 g/kg DW), followed by the tetramer hopeaphenol and the monomers *E*-resveratrol and *E*-piceatannol (0.9, 0.8, and 0.7 mg/kg DW, respectively) with a total stilbene content until 8.5 g/kg DW (Lambert et al. 2013). Similarly, Gabaston et al. (2019) showed that the main compounds in canes from eight different grape varieties were *E*-resveratrol, with values between 0.3 and 4.4 g/kg DW, and *E*-ε-viniferin, with contents between 1.3 and 4.0 g/kg DW (Gabaston et al. 2019).

Another study focused on the analysis of grapevine cane from *V. vinifera* used for table grape consumption (cultivars Crimson seedless, Flame seedless, Ohanes and Thompson seedless) (Guerrero et al. 2016). The predominant stilbene was *E*-ε-viniferin followed by the monomer *E*-piceatannol or the tetramer hopeaphenol. Among these four grape varieties, the total stilbenes in the grapevine canes oscillated between 3.0 and 4.0 mg/kg DW.

Moreover, Guerrero et al. (2016) worked on the characterization of grapevine canes from *V. vinifera sylvestris*, which is considered to be the ancestor of the present grapevine cultivars. Among the four cultivars studied, the total stilbene content ranged between 3.5 g/kg DW and 4.6 g/kg DW. Regarding the composition, *E*-ε-viniferin was the predominant stilbene in three cultivars while the dimer ampelopsin A was the predominant stilbene in one. Following these compounds, hopeaphenol was also abundant, as were *E*-resveratrol and *E*-piceatannol (Guerrero et al. 2016).

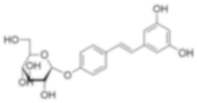
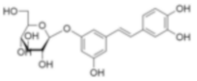
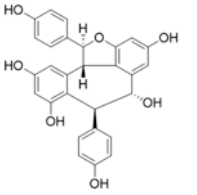
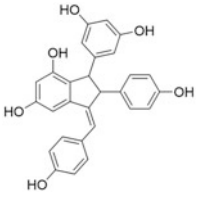
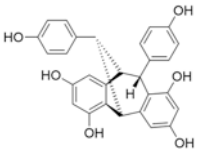
Finally, various studies have investigated the stilbene composition of grapevine cane from American and Asian wild *Vitis* species. Often used due to their resistance to a wide range of stress in crossbreeding programs, the wild *Vitis* represent a good source of stilbenes. Pawlus et al. (2013) worked on two Asian species and ten American cultivars. The stilbene content in cane varied widely depending of wild *Vitis*, with highest values in *V. riparia*, *V. amurensis*, *V. rupestris*, and *V. arizonica* (>12.1 mg/kg DW) and lowest values in *V. berlandieri*, *M. rotundifolia*, and

Table 12.1 Name, structure, and concentrations of the main stilbenes present in *Vitis* wastes

Compounds	Structure	Concentrations (mg/kg DW)	References
E- and Z-resveratrol		Cane: 190–6533	Vergara et al. (2012), Pawlus et al. (2013), Lambert et al. (2013), Guerrero et al. (2016), Gabaston et al. (2019), Escobar-Avello et al. (2021a) and Noviello et al. (2022)
		Stem: 11–3200	Bavaresco et al. (1997), Püssa et al. (2006), Anastasiadi et al. (2012), Piñeiro et al. (2013, 2017), Németh et al. (2017), Ewald et al. (2017) and Ferreyra et al. (2021)
		Leaves: 0–286 (FW)	Jean-Denis et al. (2006), Choi (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 0–3600	Martin et al. (2009) and Gabaston et al. (2019)
		Root: 61–2600	Bavaresco et al. (2003), Ji et al. (2014), Esatbeyoglu et al. (2016), Németh et al. (2017) and Gabaston et al. (2019)
E-piceatannol		Cane: 72–1962	Vergara et al. (2012), Pawlus et al. (2013), Lambert et al. (2013), Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: 12–160	Piñeiro et al. (2013, 2017)
		Leaves: 0–28 (FW)	Jean-Denis et al. (2006), Choi (2011) and Vezzulli et al. (2019)
		Trunk: 100–600	Gabaston et al. (2019)
		Root: 0–900	Gabaston et al. (2019)
Pterostilbene		Cane: ND	
		Stem: ND	
		Leaves: 0–8 (FW)	Jean-Denis et al. (2006) and Vrhovsek et al. (2012)
		Trunk: ND	
		Root: ND	
E- and *Z*-piceid		Cane: 0–100	Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: 14.5	Németh et al. (2017)
		Leaves: 0–2317 (FW)	Choi (2011), Vrhovsek et al. (2012), Wei et al. (2016), Chitarrini et al. (2017) and Vezzulli et al. (2019)

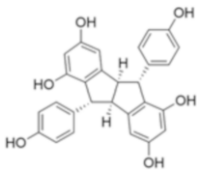
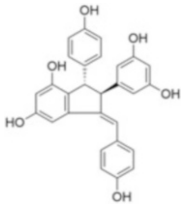
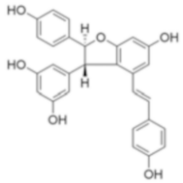
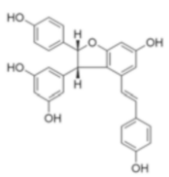
(continued)

Table 12.1 (continued)

Compounds	Structure	Concentrations (mg/kg DW)	References
		Trunk: 100–300	Gabaston et al. (2019)
		Root: 100–600	Kim et al. (2014), Wei et al. (2016) and Gabaston et al. (2019)
E- and *Z*-resveratroloside		Cane: 0–943	Pawlus et al. (2013)
		Stem: NQ	Püssa et al. (2006)
		Leaves: 0–593 (FW)	Choi (2011)
		Trunk: ND	
		Root: NQ	Aja et al. (2019)
E- and *Z*-astringin		Cane: NQ	Loupit et al. (2020)
		Stem: ND	
		Leaves: 0–62 (FW)	Jean-Denis et al. (2006), Choi (2011) and Chitarrini et al. (2017)
		Trunk: 0.0025–0.024	Rusjan et al. (2017)
		Root: ND	
Ampelopsin A		Cane: 0–1400	Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 400–2200	Gabaston et al. (2019)
		Root: 400–5300	Gabaston et al. (2019)
Ampelopsin D		Cane: ND	
		Stem: ND	
		Leaves: 0–34 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: ND	
		Root: ND	
Ampelopsin F		Cane: 0–100	Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 100–400	Gabaston et al. (2019)
		Root: 100–300	Gabaston et al. (2019)
Pallidol		Cane: 100–500	Gabaston et al. (2019) and Escobar-Avello et al. (2021a)
		Stem: ND	
		Leaves: 0–53 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)

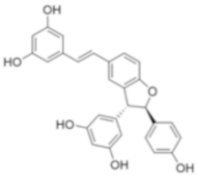
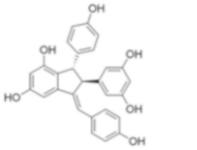
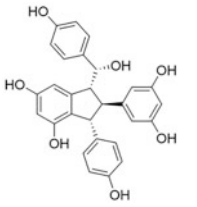
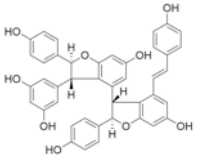
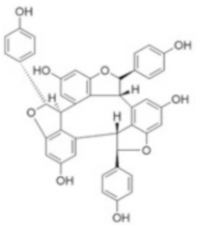
(continued)

Table 12.1 (continued)

Compounds	Structure	Concentrations (mg/kg DW)	References
		Trunk: 200–1100	Gabaston et al. (2019)
		Root: 100–700	Kim et al. (2014) and Gabaston et al. (2019)
E-parthenocissin A		Cane: 0–300	Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 100–400	Gabaston et al. (2019)
		Root: 200–600	Gabaston et al. (2019)
E-ε-viniferin		Cane: 75–10,552	Vergara et al. (2012), Pawlus et al. (2013), Lambert et al. (2013), Guerrero et al. (2016), Gabaston et al. (2019), Ferreyra et al. (2020), Escobar-Avello et al. (2021a) and Noviello et al. (2022)
		Stem: 14–2990	Bavaresco et al. (1997), Püssa et al. (2006), Anastasiadi et al. (2012), Piñeiro et al. (2013, 2017), Barros et al. (2014), Dias et al. (2015), Németh et al. (2017), Ewald et al. (2017) and Ferreyra et al. (2021)
		Leaves: 0–98 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Wei et al. (2016), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 100–7700	Martin et al. (2009), Amalfitano et al. (2011), Lambert et al. (2012), Rusjan et al. (2017) and Gabaston et al. (2019)
		Root: 500–18,000	Wei et al. (2016) and Gabaston et al. (2019)
E-ω-viniferin		Cane: 0–800	Pawlus et al. (2013), Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: 0–127 (FW)	Jean-Denis et al. (2006), Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)

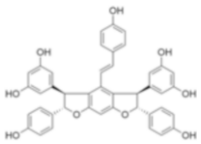
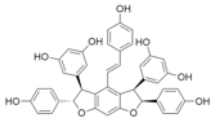
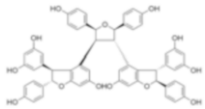
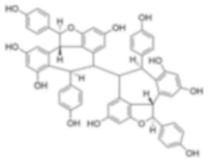
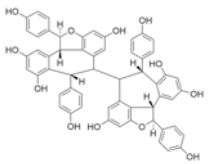
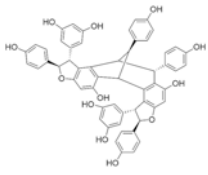
(continued)

Table 12.1 (continued)

Compounds	Structure	Concentrations (mg/kg DW)	References
		Trunk: 200–1400	Gabaston et al. (2019)
		Root: 100–400	Gabaston et al. (2019)
E-δ-viniferin		Cane: NQ	Loupit et al. (2020)
		Stem: ND	
		Leaves: NQ	Jean-Denis et al. (2006)
		Trunk: ND	
		Root: 50	Wei et al. (2016)
Quadrangulin A		Cane: ND	
		Stem: ND	
		Leaves: 0–34 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: ND	
		Root: ND	
Leachianol G		Cane: ND	
		Stem: ND	
		Leaves: ND	
		Trunk: 0.35–0.80	Amalfitano et al. (2011)
		Root: ND	
E-and Z-miyabenol C		Cane: 0–700	Lambert et al. (2013), Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: 0–270 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 200–700	Lambert et al. (2012) and Gabaston et al. (2019)
		Root: 100–300	Esatbeyoglu et al. (2016) and Gabaston et al. (2019)
α-viniferin		Cane: NQ	Loupit et al. (2020)
		Stem: ND	
		Leaves: 0–120 (FW)	Jean-Denis et al. (2006), Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 4700	Amalfitano et al. (2011)
		Root: ND	

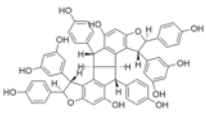
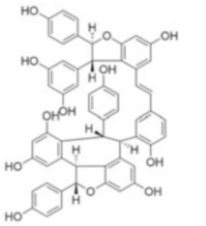
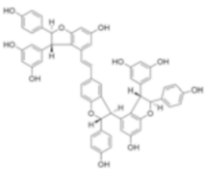
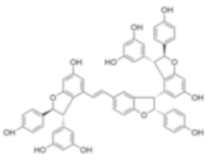
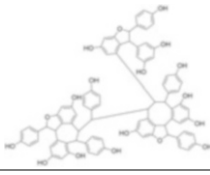
(continued)

Table 12.1 (continued)

Compounds	Structure	Concentrations (mg/kg DW)	References
E-ampelopsin E		Cane: 0–1615	Pawlus et al. (2013) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 0–200	Gabaston et al. (2019)
		Root: 0–1600	Gabaston et al. (2019)
E-amurensin B		Cane: 0–567	Pawlus et al. (2013)
		Stem: ND	
		Leaves: ND	
		Trunk: ND	
		Root: ND	
Viniferol E		Cane: 0–200	Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 100–1500	Gabaston et al. (2019)
		Root: 100–1800	Gabaston et al. (2019)
Hopeaphenol		Cane: 100–1468	Lambert et al. (2013), Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 400–2300	Lambert et al. (2012) and Gabaston et al. (2019)
		Root: 900–6800	Gabaston et al. (2019)
Isohopeaphenol		Cane: 0–3600	Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: ND	
		Leaves: 0–1311	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 200–4800	Amalfitano et al. (2011) and Gabaston et al. (2019)
		Root: 200–4600	Gabaston et al. (2019)
Vaticanol C		Cane: ND	
		Stem: ND	
		Leaves: 0–227 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: ND	
		Root: ND	

(continued)

Table 12.1 (continued)

Compounds	Structure	Concentrations (mg/kg DW)	References
Ampelopsin H		Cane: 0–600	Gabaston et al. (2019)
		Stem: ND	
		Leaves: 0–227 (FW)	Mattivi et al. (2011), Vrhovsek et al. (2012), Chitarrini et al. (2017) and Vezzulli et al. (2019)
		Trunk: 100–500	Amalfitano et al. (2011) and Gabaston et al. (2019)
		Root: 100–500	Gabaston et al. (2019)
r2-viniferin (vitisin A)		Cane: 0–200	Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 100–600	Gabaston et al. (2019)
		Root: 600–7000	Gabaston et al. (2019)
r-viniferin (vitisin B)		Cane: 0–1116	Lambert et al. (2013), Guerrero et al. (2016) and Gabaston et al. (2019)
		Stem: 6–61	Piñeiro et al. (2013)
		Leaves: ND	
		Trunk: 600–3300	Gabaston et al. (2019)
		Root: 3000–24,300	Gabaston et al. (2019)
Vitisin C		Cane: 0–100	Gabaston et al. (2019)
		Stem: ND	
		Leaves: ND	
		Trunk: 0–200	Gabaston et al. (2019)
		Root: 200–1000	Gabaston et al. (2019)
Viniphenol A		Cane: NQ	Papastamoulis et al. (2014)
		Stem: ND	
		Leaves: ND	
		Trunk: ND	
		Root: ND	

V. betulifolia (<6.2 mg/kg DW) (Pawlus et al. 2013). Depending on the species, the main compounds were the monomer *E*-resveratrol, the dimer *E*-ε-viniferin, or the tetramer r-viniferin. Recently, another study also investigated the stilbene composition of grapevine cane from 14 wild *Vitis*. The stilbene content reached 2.9 g/kg FW in *V. thunbergii*, 2.8 g/kg FW in *V. rupestris*, and 2.0 g/kg FW in *V. longyi* and

V. riparia (Loupit et al. 2020). A high *E*-ε-viniferin content was reported, the average amount being 0.9 g/kg FW and reaching a high of 2 g/kg of FW (Loupit et al. 2020).

12.2.2 Factors Modulating Stilbene Biosynthesis in Canes

12.2.2.1 Genetic Factors

As previously mentioned, the constitutive concentration of stilbenes in grapevine cane is mainly influenced by the grape variety as a result of genetic inherence. As demonstrated by various authors, some cultivars may be considered to be the highest stilbene producers, namely, Pinot Noir, Tannat, Cabernet Sauvignon, and Gewurztraminer (Lambert et al. 2013; Guerrero et al. 2016; Gabaston et al. 2019; Escobar-Avello et al. 2021a). In this sense, to obtain a maximum stilbene concentration, manufacturers can turn to these different grape varieties which are accessible in different wine regions.

Recently, Besrukow et al. (2022) investigated the intravarietal variability of stilbene content in grapevine cane by studying 13 different clones of Pinot Noir and Riesling cultivars. Regarding the clones of cv. Pinot Noir, the total stilbene content was relatively stable (average 6.1 g/kg DW), while the stilbene composition differed slightly as a result of variations in *E*-ε-viniferin and *E*-resveratrol (Besrukow et al. 2022). Focusing on the cv. Riesling clones, the study exhibited a wide variation in both composition and total stilbene content (from 3.2 g/kg up to 6.5 mg/kg DW), highlighting a significant genetically driven intracultivar variability. Taking into account inter- and intravariability, grapevine breeding programs could have an important impact on the quantity of the stilbenes in grapevine cane.

In addition to grape varieties and clones, rootstock grafting also seemed to influence the stilbene content in grapevine cane. Since the nineteenth century, the cultivated grapevine *V. vinifera*, which confers quality to the fruit, is grafted to wild *Vitis* rootstocks, which are more resistant to biotic (phylloxera) and abiotic (drought, salinity) stresses. Planted in the same vineyard, thereby avoiding any soil influence, Gabaston et al. (2019) showed that the Cabernet Sauvignon grape variety grafted onto two different rootstocks (101–14 Millardet et Grasset and 4010 Castel) exhibited a noticeable difference in both the *E*-resveratrol content and total stilbene quantity (8.5 g/kg vs. 6.5 g/kg DW) (Gabaston et al. 2019).

12.2.2.2 Environmental Factors

Environmental factors could also play a key role in stilbene level modulation. These factors include a set of stresses independent of human activity which include biotic (pathogens) and abiotic (temperature, humidity, UV) factors as well as spatial-temporal variability.

Focusing on biotic stress, vineyards are particularly subject to fungal (*Botrytis cinerea*, *Erysiphe necator*) and oomycete (*Plasmopara viticola*) attacks during the growing season. In this sense, Houillé et al. (2015) investigated the stilbene composition in vine cane during a downy mildew infection in the vineyard. The authors showed a significant alteration of stilbene profiles in cane between the non-infected and infected vineyards. The concentration of *E*-resveratrol decreased, whereas *E*-ε-viniferin increased. Regarding minor compounds, the content of *E*-piceatannol, ampelopsin A, and r-viniferin dropped, while the levels of miyabenol C and isohopeaphenol increased in downy mildew-infected vineyards (Houillé et al. 2015). These findings suggest a tendency of grapevine cane to produce oligomerized compounds to defend themselves against biotic pressure. Further studies demonstrated then that the main active compounds against vineyard pathogens were the more complex stilbenes such as dimers (*E*-ε-viniferin), trimers (miyabenol C), and tetramers (r2-viniferin, r-viniferin, hopeaphenol, isohopeaphenol), providing support to the first postulates (Schnee et al. 2013; Gabaston et al. 2017; El Khawand et al. 2020).

The stilbene levels in grapevine cane may also be modulated by abiotic factors, in particular variations in climatic conditions such as temperature, solar radiation, evapotranspiration, and humidity/rainfall. Guerrero et al. (2016) investigated these influential factors related to the individual and total stilbene contents in grapevine cane during a 3-year study. The authors demonstrated that high humidity and rainfall with a minimum temperature, solar radiation, and evapotranspiration were correlated with a high content of r2-viniferin, *E*-ε-viniferin, and *E*-ω-viniferin in cane (Guerrero et al. 2016). Several authors also reported that high relative humidity and mild temperatures were suitable factors for the development of vineyard disease, and therefore a modification of stilbene content in grapevine canes (Bavaresco et al. 2003; Tříska et al. 2017; Gabaston et al. 2020).

The temporal variability of the stilbene content in the vine canes was also investigated by Besrukow et al. (2022) by means of studying the pruning time (3 different months) and the effect of vintage (3 different years) (Besrukow et al. 2022). It appeared that the highest amount of stilbenes in grapevine cane was found in the samples pruned in December (compared to October and February) in every vintage, which meant a monthly scale temporal variability (Besrukow et al. 2022). These results were in agreement with those of De Bona et al. (2020), who showed an increase in stilbenes in vine cane from October to December (De Bona et al. 2020). Moreover, both the stilbene profile and content varied widely depending on the year (2017, 2018, and 2019). These results were in agreement with previous studies which reported a vintage variability in the stilbene level in grapevine canes (Guerrero et al. 2016; Tříska et al. 2017).

12.2.2.3 External Factors (Human Management)

The influence of human practices could also modulate the quantities of stilbenes in grapevine cane, in particular post-pruning management such as storage conditions (duration, temperature), or mechanical stress.

Gorena et al. (2014) investigated the post-pruning process by storing grapevine canes for 8 months at room temperature. The concentration of stilbenes in grapevine cane varied widely during storage with a significant increase after 2 months and a maximum at the third month, a fivefold increase in the initial stilbene concentration being found (Gorena et al. 2014). Cebrian et al. (2017) confirmed these results by highlighting a maximum stilbene content at the third month followed by constant concentrations until the sixth month (Cebrián et al. 2017). A recent study mentioned that long-term storage for 1–3 years leads to a drop in the stilbene concentration (Soural et al. 2019). Houillé et al. (2015) studied the post-pruning process of vine cane by adding another variable: the storage temperature. The grapevine canes were stored for 10 weeks at −20, 5, 15, 20, and 28 °C in the dark (Houillé et al. 2015). When the canes were stored at 15 or 20 °C, the concentration of *E*-resveratrol gradually increased with a maximum at 6 weeks. At 5 °C, the increase was slower, while at 28 °C the concentration did not reach a similar amount as at 5, 15, and 20 °C. Regarding extreme conditions at −20 °C and a short heat-shock treatment (2 h at 65 °C), no *E*-resveratrol was measured (Houillé et al. 2015). Besides, Sáez et al. (2018) investigated another parameter of storage: the relative humidity at 60 or 70% for 134 days after pruning. The results showed a determining effect of the relative humidity on the content of *E*-resveratrol and *E*-piceatannol, with higher concentrations at a relative humidity of 60% than at 70% (Sáez et al. 2018). Overall, these different studies suggest that 6 weeks of post-pruning storage coupled to a temperature between 15 and 20 °C is enough to reach a maximum stilbene production in grapevine cane.

Furthermore, another work investigated the influence of mechanical stress on the stilbene content in vine cane. A mechanical wounding on freshly pruned canes was performed with sections lengths of 0.2, 0.5, 1, 5, and 10 cm followed by storage for 28 days at 20 °C. Cutting the grapevine canes into short segments immediately after pruning promoted an increase in *E*-resveratrol and *E*-piceatannol content (Billet et al. 2018). Moreover, the production levels were proportional to the segment length, with the exception of the 0.2 section. Overall, mechanical stress did not result in a better stilbene accumulation than other storage conditions, but significantly shortened the time required to reach the maximum stilbene concentration (Billet et al. 2018).

To resume the influence of external factors, the stilbene content from vine cane could be improved by cutting the freshly pruned canes to a length of 0.5 cm before storage at 15–20 °C for at least 2 weeks.

12.2.3 Application of Cane Biomass in Agri-Food Industry

12.2.3.1 Agriculture

Known as phytoalexins, stilbenes from grapevine cane extracts were investigated in the area of agriculture, especially their use as a natural fungicide, oomycide, and insecticide. One study analyzed the effects of *V. vinifera* canes extracts against the major vineyard pathogens such as downy (*P. viticola*) and powdery (*E. necator*) mildews and gray mold (*B. cinerea*). Applied at a concentration of 1000 mg/L against mildews and 5000 mg/L against gray mold, the extracts showed significant in vitro antifungal activity with inhibition of zoospore mobility and sporulation of *P. viticola*, inhibition of conidia germination of *E. necator*, and inhibition of mycelium growth of *B. cinerea* (Schnee et al. 2013). A larger-scale study led by Richard et al. (2016) performed in vivo experiments on grape plants. A grapevine cane extract at 5000 mg/L was tested against downy mildew in a greenhouse and in the vineyard. After the treatments in the greenhouse, the disease reduction ranged from 59 to 69% for pathogen attack frequency and from 83 to 88% for infected leaf surface. In the vineyard assay, treating plants every seventh day reduced the frequency of attack by between 16 and 39% and leaf surface infection by between 57 and 61% (Richard et al. 2016). While the values obtained in the greenhouse assays were similar to the phytosanitary products usually used, the results obtained in the vineyard were quite inferior to the current product, i.e., copper treatment. A recent study also evaluated the in-field potential of grape cane extract (8000 mg/L) against *P. viticola* on three sensitive cultivars over 3 years. A mean reduction in disease incidence of 35% on leaves and 38% on bunch stems was obtained as well as a mean reduction in disease severity of 35% on leaves and 43% on grape clusters (Billet et al. 2019). Similarly, the authors showed the potential of grapevine cane extract to control downy mildew, but also concluded that the extract appeared less efficient than copper treatment (at 4000 mg/L). It should also be noted that no phytotoxicity and adverse effects on auxiliary fauna such as earthworm or mite were reported using grapevine cane extracts (Billet et al. 2019). Recently, El Khawand et al. (2020) proposed a chemical process based on oxidative coupling, using metals to increase the oligostilbene rate and the in vitro biological effectivity of cane extract against grapevine pathogens. The processed extract, which contains newly described stilbenes, proved to be threefold more active than the initial extract against *P. viticola* ($IC_{50} = 63$ mg/L and 197 mg/L, respectively) and at least 40-fold more active against *B. cinerea* ($IC_{50} = 5$ mg/L and >200 mg/L, respectively) (El Khawand et al. 2020).

Furthermore, another study investigated the use of grapevine cane extract as a botanical insecticide against *Spodoptera littoralis* larvae, which is one of the most destructive agricultural lepidopteron pests within its subtropical and tropical range (grasses, legumes, crucifers, and deciduous fruit trees). The results showed a chronic toxicity of the extract with lethal concentrations at 50% at 164μg/cm^2 (Pavela et al. 2017).

Overall, stilbene-enriched extracts from grapevine cane appear to be a tool to complement or replace the current treatments for various vineyard pathogens or crop pests. While further research is needed, especially terms of in-field treatment, the valorization of these viticultural by-products in agricultural area are promising.

12.2.3.2 Oenology

In addition to being effective antioxidants, stilbenes are known to possess antimicrobial properties, and some researchers have investigated the potential uses of stilbene-enriched cane extract as wine preservative to replace the traditionally used product sulfur dioxide (SO_2), which has been linked with several human health risks (Guerrero and Cantos-Villar 2015; Cruz et al. 2018).

One study investigated the use of a commercial grapevine cane extract (Vineatrol®) containing 29% stilbenes as a preservative in red wine. At bottling, the most important oenological parameters (ethanol, pH, acetic, malic and succinic acids, ethyl acetate, etc.) were good. The wines treated with the extract showed a purer color than the SO_2 treated wines and obtained high scores in the sensory analysis (Raposo et al. 2016). However, after 12 months of storage, the wines treated with the extract showed signs of oxidation (Raposo et al. 2016). Raposo et al. (2018) continued this investigation by testing two concentrations of the same cane extract (50 and 100 mg/L) and evaluating the impact on the wine quality (Raposo et al. 2018). The results showed that the extract was able to stabilize wine color with a higher intensity and darker hue, which was promoted by a polymerization between anthocyanins and other wine constituents. Ruiz-Moreno et al. (2018) also tested the two concentrations of cane extract and evaluated the effect on the aromatic profile of wine. If the quality of the wines was not negatively affected, variations in some aroma compounds (β-damascenone, isoeugenol) and odorant zones were reported as well as an increase of the astringency sensation (Ruiz-Moreno et al. 2018). A similar investigation was applied to the production of white wine using grapevine the same cane extract instead of SO_2 (Cruz et al. 2018). The extract inhibited the malolactic fermentation (which is desirable in white wines), preserved methionol (which can give a cooked potatoes scent by oxidation), and generated a decrease in acetaldehyde content (Cruz et al. 2018). However, after 6 months of storage in the bottle, some side effects were observed in color and sensory properties. To prevent undesirable effects, Gutiérrez-Escobar et al. (2021) recently developed a pure stilbene extract (99% of total stilbenes, with 70% of *E*-ε-viniferin and 18% of *E*-resveratrol) from grapevine cane through purification steps using centrifugal partition chromatography (Gutiérrez-Escobar et al. 2021). Contrary to the previous non-purified cane extract, this stilbene-enriched cane extract did not affect the volatile profile of wines. The extract also showed antimicrobial activity against yeast and bacteria, mainly against *Brettanomyces* (Gutiérrez-Escobar et al. 2021). The toxicological investigation by Medrano-Padial et al. (2021) on this extract demonstrated that grapevine cane extract appeared to be safe for its use in wines, although further in vivo studies are needed to unequivocally determine its safety (Medrano-Padial et al. 2021).

Furthermore, grapevine canes have been tested as toasted chips or granules in the winemaking process (Cebrián-Tarancón et al. 2018, 2019). Toasted in an air circulation oven at 180 °C for 45 min, the grapevine shoot chips (or granules) were added before or after the alcoholic fermentation or after the malolactic fermentation. The maceration occurred for 35 days, and the results showed significant differences in the phenolic acid concentration and stilbene content in the treated wines. Moreover, it could be noted that the time of addition of the grapevine shoots did not influence the results. Overall, these findings confirmed that the addition of grapevine canes chips to wines can modulate their chemical compositions when compared with their respective control wines.

12.2.3.3 Medicine

If individual stilbenes have already demonstrated significant effects on several human health disorders, the use of grapevine cane extract as an association of a number of stilbenes with potential synergistic activities is promising.

One study worked on the effect of grapevine cane extracts on leukemic cells which possessed a resistance to programmed cell death (Billard et al. 2002). The cane extracts demonstrated in vitro antiproliferative and apoptotic effects through several mechanisms. Similarly, Marel et al. (2008) highlighted the in vitro antitumoral activities of grapevine cane extract on human adenocarcinoma colon cells, inhibiting cell proliferation and stopping the cell cycle in S phase, which induced an apoptotic process (Marel et al. 2008). Following the detection of the carcinogenic potential of stilbenes, a study showed that cane extract (at 2.4 mg/L) was able to reduce the number of malignantly transformed foci in chemically induced BALB/c-3T3 cells (Müller et al. 2011). Recently, Empl et al. (2018) investigated the consumption of grapevine cane extract to prevent cancers of the gastrointestinal tract. In vitro and in vivo assays highlighted a reduction of the number of adenoma in male mice and adenoma volume in female mice at a low (2.3 mg/kg diet) or high dose (476 mg/kg diet) (Empl et al. 2018).

Furthermore, several authors have studied the potent antioxidative effect of grapevine cane extracts. Müller et al. (2009) demonstrated the ability of a cane extract to scavenge free radicals, to inhibit lipid peroxidation, and to enhance glutathione peroxidase and superoxide dismutase gene promoter activities (Müller et al. 2009). Other authors also showed an antioxidant activity of grapevine cane extract as well as its main compounds in ORAC or DPPH assays (Biais et al. 2017; Gharwalová et al. 2018).

Aiming to discover neuroprotective chemicals, Biais et al. (2017) investigated the cytoprotective effect of a grapevine cane extract on pheochromocytoma cells (PC12 cell line) treated with the beta-amyloid peptide (Aβ). The Aβ is considered to be responsible for Alzheimer's disease. The authors showed that the addition of a grapevine cane extract makes it possible to prevent the in vitro cytotoxicity induced by the Aβ, and even increase the cell viability in dose-dependent manner. Regarding the pure compounds, the most efficient stilbenes as inhibitors of Aβ toxicity were the monomer piceatannol and the dimer ampelopsin A (Biais et al. 2017).

The application of plant extracts such as grapevine cane was frequently limited by their poor solubility and stability in aqueous solution. To counteract these undesirable effects, the encapsulation of grapevine cane extract in hydroxypropyl beta-cyclodextrin and maltodextrin, highly biocompatible and approved by the Food and Drug Administration, was recently investigated (Escobar-Avello et al. 2021b). Regarding the encapsulation efficiency of stilbenes, the values oscillated between 32.7 and 97.0% with a mean value of 78.6%. The lowest efficiency value was obtained for *E*-resveratrol and the highest for restrytisol. The antioxidant activity of the encapsulated extract was also investigated and exhibited similar results to the non-inclusion complex (Escobar-Avello et al. 2021b).

To sum up, the use of grapevine cane extract has demonstrated encouraging results with regard to its antioxidant, chemopreventive, and neuroprotective activities, allowing it to be considered for use in medicinal and pharmaceutical treatments. The encapsulation process could also be envisioned in order to improve the solubility, stability, and bioavailability of the cane extract.

12.2.3.4 Food

Some recent research has proposed the use of grapevine cane extract as sustainable food packaging material to prevent the microbial contamination of food. These studies were based on the antimicrobial properties of stilbenes and could represent a potential green source of natural additives.

In fact, Kodeš et al. (2021) have recently studied the antimicrobial activity of a grapevine cane extract against *Candida* biofilm. As many pathogenic microorganisms have developed resistance to antibiotics, the search for treatments has turned to plant extracts, which contain a pool of compounds with multi-factorial targets. The highest inhibition of metabolic activity and biofilm biomass was obtained in *C. albicans* and *C. krusei* biofilms after treatment with the cane extract at 30 mg/L (Kodeš et al. 2021).

Thus, one study investigated the combination of a grapevine cane extract with a thermoplastic starch-based material (Díaz-Galindo et al. 2020a). Starch is an abundant, sustainable, and easily processed biopolymer from corn, wheat, or potato. However, it is sensitive to degradation caused by moisture and aging. In this sense, the biomaterial prepared with the grapevine cane extract was subjected to thermal, mechanical, antioxidant, and antimicrobial assays. While the thermal stability of the biomaterial was not influenced by the incorporation of cane extract, its mechanical resistance decreased, and it presented high antioxidant ability. Regarding the effect against foodborne microorganisms, the cane extract-based material exhibited an inhibition against *B. cinerea* and *Staphylococcus aureus*, whereas no activity was noted against *Salmonella typhimurium* and *Escherichia coli* (Díaz-Galindo et al. 2020a).

Similarly, another study analyzed the loading of a grapevine cane extract with a poly(lactic acid) (PLA)-based films. Lactic acid originated from renewable sources of sugar such as sugarcane, corn, wheat, or cassava root (Díaz-Galindo et al. 2020b).

The inclusion of grapevine cane aimed at making packages and food products biologically safe. The findings demonstrated that the loading of 10% of cane extract resulted in decreased tensile strength and increased the elongation at break. Moreover, the thermal stability increased, as did the water vapor barrier. Regarding antifungal and antimicrobial activities, a growth inhibition of *B. cinerea* was obtained in the range of 15–35%, while an inhibition of adhesion was exhibited against several foodborne microorganisms such as *Pseudomonas aeruginosa*, *Pectobacterium carotovorum*, *Saccharomyces pastorianus*, and *Listeria monocytogenes* (Díaz-Galindo et al. 2020b).

12.2.3.5 Cosmetics

Regarding the potential application of grapevine cane in the cosmetics area, some authors have focused on the effect on the skin aging process through tyrosinase inhibition. In fact, the tyrosinase enzyme is involved in the skin pigmentation process by modulating the presence of melanin, an excess and uncommon distribution of which can cause dark spots, or even increase the risk of melanoma. In this sense, to avoid any aesthetic or human health problems, the search of tyrosinase inhibitors has attracted great interest in the cosmetics and medicine industries (Honisch et al. 2020). Malinowska et al. (2020) showed that cane extracts and pure stilbenes (*E*-resveratrol and *E*-ε-viniferin) were active tyrosinase inhibitors with inhibition values oscillating between 39.5 and 76.0% (Malinowska et al. 2020). In addition, these authors studied the delaying of skin aging processes through the activation of natural cell repairing mechanisms such as sirtuin (SIRT) activating compounds (Malinowska et al. 2020). Most of the cane extracts tested from various grape varieties showed a significant SIRT1 activation with values ranging between 142 and 171%. Moreover, the pure stilbenes also significantly stimulated SIRT1 activation with a dose-response effect (Malinowska et al. 2020).

Furthermore, another work determined the potential adverse effects of grapevine cane extract against different kinds of skin cell types such as keratinocytes (HaCaT cell line) and fibroblasts (HFF-1 cell line), which represent the epidermal and dermal layers, respectively. The results showed an absence of cytotoxicity of cane extracts in concentrations below 100μg/mL in HaCaT cells and 1000μg/mL in HFF-1 cells (Moreira et al. 2020). Moreover, the authors tested the stability of a cane extract prepared in a topical formulation through various physical characteristics such as pH, color, texture, and rheological behavior. The pH appeared to be close to the skin pH (4.8), ensuring its compatibility to be employed in cosmetic products; the gel formulation showed a dark color with red and yellow trends, a texture with a low firmness, good adherence, and good viscosity (Moreira et al. 2020).

On the whole, grapevine cane extract demonstrated promising results for topical skin formulations with the capacity to modulate the whitening via tyrosinase inhibition and to slow down cellular senescence using sirtuin activation, representing an interesting value in the cosmetics industry.

The main applications of grapevine cane extracts are resumed in Table 12.2.

Table 12.2 Main applications of grapevine cane extracts

Cane extracts				
Agriculture	Oenology	Medicine	Cosmetic	Food
– Anti-mildew – Antifungal – Insecticide	– Alternative to SO_2 – Kind of chips	– Antioxidant – Chemopreventive/anticancer agent – Neuroprotective	– Tyrosinase inhibition – Cell repairing mechanisms through stimulator of SIRT1	– Food packaging – Antimicrobial
Schnee et al. (2013), Richard et al. (2016), Gabaston et al. (2017), Pavela et al. (2017), Billet et al. (2019) and El Khawand et al. (2020)	Raposo et al. (2016, 2018), Cebrián-Tarancón et al. (2018, 2019), Cruz et al. (2018), Ruiz-Moreno et al. (2018), Gutiérrez-Escobar et al. (2021) and Medrano-Padial et al. (2021)	Billard et al. (2002), Marel et al. (2008), Müller et al. (2011), Biais et al. (2017), Empl et al. (2018), Gharwalová et al. (2018), Escobar-Avello et al. (2021b) and Kodeš et al. (2021)	Honisch et al. (2020), Malinowska et al. (2020) and Moreira et al. (2020)	Díaz-Galindo et al. (2020a, b)

12.3 Vine Wastes: Stems

12.3.1 Stilbene Composition in Grapevine Stems

One of the first studies characterizing the stilbene level in grapevine stems was conducted by Bavaresco et al. (1997), which aimed to discover possible sources of resveratrol. Obtained after destemming, grape stems from eight different cultivars were analyzed. Depending on the grape varieties, the authors demonstrated the predominance of *E*-resveratrol with a content between 31 and 393 mg/kg DW, followed by *E*-ε-viniferin with a content between 34 and 171 mg/kg DW, and *Z*-resveratrol with a content between 0.1 and 0.59 mg/kg DW (Bavaresco et al. 1997). Later, other authors confirmed the main presence of *E*-resveratrol and *E*-ε-viniferin in Greek, Italian, and Portuguese cultivars (Makris et al. 2008; Spatafora et al. 2013; Barros et al. 2014; Ferreyra et al. 2021). Anastasiadi et al. (2012) compared their content in stem from red and white grape varieties, showing respective *E*-resveratrol levels of 149 and 113 mg/kg DW, and respective *E*-ε-viniferin levels of 314 and 288 mg/kg DW. These values were, therefore, in agreement with original findings (Anastasiadi et al. 2012) (Table 12.1).

Some authors found the highest stilbene content in vine stems, namely, Püssa et al. (2006), who showed *E*-resveratrol values between 100 and 3200 mg/kg DW and *E*-ε-viniferin values between 700 and 1700 mg/kg DW in Estonian cultivars. Meanwhile, Dias et al. (2015) reported *E*-ε-viniferin content of 2990 mg/kg DW in Portuguese cultivars (Püssa et al. 2006; Dias et al. 2015).

In addition to *E*-resveratrol and *E*-ε-viniferin, several authors tried to decipher other stilbene compounds in grapevine stems. The monomer *E*-piceatannol was identified and quantified in the Syrah cultivar with a content oscillating between 16.6 and 21.1 mg/kg DW (Piñeiro et al. 2013). Later, the same authors found *E*-piceatannol in four white and 11 red *V. vinifera* cultivars (values between 12 and 160 mg/kg DW) (Piñeiro et al. 2017). The monomer *E*-piceid was also characterized in grapevine stems (cv. Merlot) with a content of 14.5 mg/kg DW (Németh et al. 2017). Another study putatively identified several stilbenes in vine stems, especially resveratrol derivatives (C- and O-glucosylated), piceatannol derivatives, and some unnamed dimers, trimers, and tetramers (Püssa et al. 2006). Finally, the tetramer r-viniferin was quantified in 21 cultivars with levels between 6.8 and 61.1 mg/kg DW (Piñeiro et al. 2013) (Table 12.1).

12.3.2 Factors Modulating Stilbene Biosynthesis in Stems

12.3.2.1 Genetic Factors

Similar to grapevine cane, the constitutive concentrations of stilbenes in vine stem vary according to the grape varieties. Regarding the most widespread white grape cultivars, the highest stilbene producers were Vijiriega (3166 mg/kg DW), Moscatel

(2081 mg/kg DW), Chardonnay (799 mg/kg DW), and Palomino fino (772 mg/kg DW). As for the red grape varieties, the cultivars Tannat (626 mg/kg DW), Zinfandel (450 mg/kg DW), and Tempranillo (375 mg/kg DW) showed the highest stilbene content (Piñeiro et al. 2013, 2017). Other autochthonous cultivars also exhibited significant amounts of stilbenes, such as Greek cultivars with values of up to 742 mg/kg DW in cv. Mandilaria (Anastasiadi et al. 2012), Portuguese cultivars with levels reaching 2990 mg/kg DW in cv. Rabigato (Dias et al. 2015), or Estonian grape varieties with contents up to 4900 mg/kg DW in cv. Hasaine sladki (Püssa et al. 2006). Moreover, it should be noted that the stilbene content varied also notably in *V. sylvestris* cultivars, with values oscillating between 47.3 and 425 mg/kg DW (Piñeiro et al. 2013, 2017).

12.3.2.2 Environmental Factors

Regarding the environmental stimuli on grapevine stems, few studies are available, especially ones analyzing the influence of biotic (pathogens) and abiotic (temperature, humidity, rainfall) factors. However, some authors have investigated vintage variability by studying stilbene levels over several years. A recent study on vine stems from Spanish cultivars in 2016 and 2018 reported slight variations in the content of *E*-resveratrol and *E*-ε-viniferin (Esparza et al. 2021). More specifically, in the Mazuelo and Tempranillo cultivars, the *E*-resveratrol level varied between 240 and 300 mg/kg extract and 40 and 70 mg/kg extract, respectively, in 2016 and 2018. Similarly, in the Mazuelo, Tempranillo, and Garnacha cultivars, the *E*-ε-viniferin content ranged between 690 and 550 mg/kg extract, 200 and 150 mg/kg extract, and 330 and 460 mg/kg extract, respectively, in 2016 and 2018 (Esparza et al. 2021). Another study on German cultivars demonstrated a wider variation in *E*-resveratrol and *E*-ε-viniferin content, depending on the vintage and wine-growing area. In 2014, the amounts of *E*-resveratrol and *E*-ε-viniferin were close to 15–25 mg/kg DW and 20–75 mg/kg DW, respectively, while in 2015 these amounts varied from 110 to 290 mg/kg DW and 80 to 250 mg/kg DW, respectively, a much higher stilbene content being found therefore in 2015 (Ewald et al. 2017).

In addition to vintage, another study investigated the variability of stilbenes in grape cluster stems during the growth cycle. From the end of July to the beginning of September, the change in stilbene content was not consistent in the different grape varieties. The *E*-resveratrol level increased in cv. Pinot blanc, remained stable in cv. Rieslaner and Riesling, and dropped after 1 month in cv. Müller-Thurgau, before finally increasing when the grapes reached full ripeness (Ewald et al. 2017).

As previously mentioned in cane, the vintage and growth cycle variabilities of stilbenes in grapevine stems could be induced by fungal attacks, insect bites, or abiotic stresses, which varied each year.

12.3.2.3 External Factors (Human Management)

Stilbene synthesis is known to be activated by exogenous stress factors, such as ultraviolet irradiation or chemical elicitors involved in the downstream production of

stilbenes (Li et al. 2006; Burdziej et al. 2021). In this sense, Piñeiro et al. (2013) artificially irradiated bunch stem with UV-C postharvest in order to stimulate the stilbene production in stem. A notable increase in *E*-piceatannol and *E*-resveratrol content in grape stems from UV-C-treated versus untreated grapes was obtained (Piñeiro et al. 2013). Moreover, the authors tried to combine a pre-harvest treatment of bunch stems with the elicitor methyl jasmonate and a post-harvest treatment with UV-C. The results showed an increase in *E*-piceatannol, *E*-resveratrol, and *E*-ε-viniferin levels in the stems in comparison with the untreated grapes or those only receiving UV-C (Piñeiro et al. 2013). Globally, these findings strongly suggest that the combination of pre- and post-harvest treatments could promote stilbene synthesis and thus produce stilbene-enriched stem extracts.

Furthermore, a recent work investigated the influence of the long-term storage of grapevine stems on stilbene content. Stored for 64 days at room temperature, the *E*-ε-viniferin level in stems of cv. Sousao and Syrah remained stable, while in cv. Tinta Barroca the concentration increased after 50 days, reaching more than 0.6 mg/kg DW (Gouvinhas et al. 2018). As previously observed in cane, post-harvest storage appeared to be beneficial to stilbene content in grapevine stems, or at least presented no adverse effects.

12.3.3 Application of Stem Biomass in Agri-Food Industry

12.3.3.1 Oenology

Focusing on red wines, the use of vine stems (50 or 75% of destemmed grapes) showed a good anthocyanins/color intensity ratio and a stable polymerization state of colored pigments after 12 months of storage (Suriano et al. 2015). However, an abusive use of stem (100% of destemmed grapes) could decrease the color intensity (Suriano et al. 2015). From a sensorial point of view, the use of grapevine stems could lead to a slight adverse sensation, particularly astringency and bitterness tastes (Pascual et al. 2016).

In an ongoing search for alternatives to SO_2, some authors have investigated the valorization of grapevine stem extracts owing to their richness in antioxidant and antimicrobial phenolic compounds. A recent study showed that substituting SO_2 with grapevine stem extract leads to wines with a phenolic composition and organoleptic properties similar to or even better than the control wine (Esparza et al. 2020). Moreover, Casquete et al. (2021) highlighted the high antioxidant and antimicrobial activities of grapevine stems, thereby guaranteeing the microbiological stability and protection of wines from oxidation (Casquete et al. 2021).

Regarding white wines, Marchante et al. (2019) investigated the chemical composition, antimicrobial activity, and sensorial properties of wines using vine stem extract. The grapevine stems displayed an antimicrobial effect similar to that of SO_2 as well as comparable sensorial properties with fruity and floral attributes (Marchante et al. 2019). The color of white wines could also be affected by a browning

tendency, but without other signs of oxidation. In addition, the total esters increased in comparison with SO_2 treated wines, which promoted aroma complexity (Marchante et al. 2019).

12.3.3.2 Medicine

Owing to their richness in phenolics, especially in stilbenes, grapevine stem extracts were evaluated for their antioxidant capacity. In vitro tests such as ABTS, ORAC, and DPPH were performed. Stem extracts showed values ranging from 0.63 to 1.17 mmol Trolox equivalent (TE)/g DW for the ABTS assay, 0.37–0.56 mmol TE/g DW for the DPPH assay, and 1.2–2 mmol TE/g DW for the ORAC assay (Leal et al. 2020a; Ferreyra et al. 2021). The grapevine stems were also able to improve the redox status of endothelial and muscle cells as well as human keratinocytes by decreasing the levels of thiobarbituric acid reactive substances, the protein carbonyl, and the reactive oxygen species (ROS) and increasing glutathione levels (Goutzourelas et al. 2015; Domínguez-Perles et al. 2016). Stem extract also displayed a protective effect of plasmid DNA against peroxyl radicals induced by oxidative modification, thereby showing an antimutagenic property (Veskoukis et al. 2020). Overall, the antioxidant capacity of grapevine stems allows their use to be considered in medicinal treatments or the development of antioxidant food supplements.

Aiming to explore medicinal applications, several authors have investigated the anticarcinogenic activity of vine stems. One study worked on the application of extracts against liver and cervical cancer cell growth. After 24 h of treatment, all the tested grape stem extracts at low concentrations inhibited cell growth with average IC_{50} values of 50 and 32 mg/L, respectively (Apostolou et al. 2013). Similarly, a treatment involving stem extracts tested for 72 h on colon, breast, thyroid, and renal cancer cells demonstrated cell proliferation inhibition, with IC_{50} values ranging from 121 to 400 mg/L (Sahpazidou et al. 2014). Regarding the chemopreventive capacity of grapevine stems, the antiangiogenic potential of extracts was tested (Stagos et al. 2014). When diseased cells produce abnormally large amounts of angiogenesis factors, excessive angiogenesis can occur. The results showed that grapevine stem extract inhibited tube formation in human endothelial cells, highlighting antiangiogenic activity. Moreover, the authors suggested that the extract may exert its activity through the inhibition of VEGF levels (Stagos et al. 2014).

12.3.3.3 Food

The antimicrobial capacity of grapevine stems was also investigated. Extracts were tested against human gastrointestinal pathogenic bacteria such as the gram-positive *S. aureus*, *Enterococcus faecalis*, and *Listeria monocytogenes* as well as the gram-negative *E. coli*, *Pseudomonas aeruginosa*, and *Klebsiella pneumoniae* (Leal et al. 2020b). Stem extracts showed high activity against *S. aureus* and *E. faecalis* and a

moderate efficiency against *L. monocytogenes* and *P. aeruginosa* (Leal et al. 2020b). The authors reported a minimal inhibitory concentration (MIC) ranging from 16 to 18 g/L against *L. monocytogenes*, *S. aureus*, *E. coli*, and *Salmonella enterica*, while other authors showed MIC values of 66.7 g/L of grapevine stem extracts against *L. monocytogenes* and *P. aeruginosa* (Dias et al. 2015; Vázquez-Armenta et al. 2017). Moreover, the grapevine stem extract at 25 g/L effectively reduced populations of bacteria inoculated in lettuce and spinach, highlighting the antimicrobial ability of vine stems against important foodborne pathogens (Vázquez-Armenta et al. 2017).

12.3.3.4 Cosmetics

Grapevine stem extracts were evaluated as tyrosinase inhibitors with the aim of mitigating hyperpigmentation, over-tanning, age spots, or melasma disorders. Used at 1 g/L, the stem extracts showed tyrosine inhibition ranging from 41.5 to 53.8% depending on the grape varieties (Leal et al. 2020a). The grapevine stem was also tested as an elastase inhibitor. Elastase is an enzyme that hydrolyses elastin, which is involved in the mechanical properties of connective tissues. The high activity of this enzyme leads to less elastin production, and therefore a loss of skin firmness and elasticity. Stem extracts showed elastase inhibition with values between 68.0 and 98.0%. Regarding the different cultivars, the Syrah grape variety presented the better inhibition activity of both enzymes analyzed, while the Tinta Roriz variety showed a lower capacity to inhibit tyrosinase and the Arinto variety to inhibit elastase (Leal et al. 2020a). Overall, the grapevine stem extracts showed anti-aging properties that affirm their potential valorization in the cosmetics industry.

The main applications of grapevine stems are shown in Table 12.3.

Table 12.3 Main applications of grapevine stem extracts

Stem extracts			
Oenology	Medicine	Food	Cosmetics
– Favorized polymerization – Color stabilization – Organoleptic properties similar to SO_2 treated wines – Antioxidant and antimicrobial activities	– Antioxidant – Antimutagenic – Chemopreventive/ anticancer agent – Antiangiogenic	– Antimicrobial	– Tyrosinase inhibition – Elastase inhibition
Suriano et al. (2015), Pascual et al. (2016), Marchante et al. (2019), Esparza et al. (2020) and Casquete et al. (2021)	Apostolou et al. (2013), Sahpazidou et al. (2014), Stagos et al. (2014), Goutzourelas et al. (2015), Domínguez-Perles et al. (2016), Leal et al. (2020a) and Ferreyra et al. (2021)	Dias et al. (2015), Vázquez-Armenta et al. (2017) and Leal et al. (2020b)	Leal et al. (2020a)

12.4 Vine Wastes: Leaves

Leaf removal in the cluster zone is a widely used practice that can be performed at veraison, during the onset of the ripening, and also post-veraison (Ćirković et al. 2022). This practice improves berry quality (for instance, pigmentation, aromatic compounds, and secondary metabolites) and reduces conditions favorable to bunch rot complex diseases (Cataldo et al. 2021). Regarding reusing the leaves as by-products, it should be taken into account that if they are harvested in late summer, after potential treatment(s) with pesticides, they should not be used for animal feed, because they could induce toxic effects. Conversely, leaves harvested during the spring before any treatment has been applied are free of pesticide residues and can be considered for use as potential health by-products. In fact, the selective removal of grapevine leaves in the spring generates large amounts of interesting by-products with multiple and diverse applications.

To date, leaves from *V. vinifera* L. constitute the least studied or valorized residue of the grape crops and the winery industry. However, this waste (coming from leaf removal) is a promising source of compounds with nutritional properties and biological potential.

12.4.1 Stilbene Composition in Grapevine Leaves

Although grapevine leaves are mainly composed of phenolic acids, flavonoids, and coumarins, more than 40 stilbenes have been reported in the leaves of *V. vinifera*, albeit at lower concentrations than both phenolic acids and flavonoids. In fact, stilbenes are often undetected in healthy leaves and are produced after biotic or abiotic stresses. The most predominant stilbenes in healthy mature leaves are monomeric stilbenes, often glycolylated as *Z*- and *E*-piceid (>2300 mg/kg FW), *Z*- and *E*-resveratroloside (>590 mg/kg FW), *Z*- and *E*-resveratrol (>280 mg/kg FW), *Z*- and *E*-astringin (>60 mg/kg FW), and *E*-piceatannol (>2300 mg/kg FW) (Choi 2011) (Table 12.1).

When grapevine leaves were infected with *P. viticola*, several complex stilbenes were identified: dimers (ampelopsin D, quadrangularin A, *Z*- and *E*-ε-viniferin, *Z*- and *E*-ω-viniferin, *Z*- and *E*-δ-viniferin, pallidol), trimers (α-viniferin, *E*-*Z*-miyabenol C, *Z*- and *E*-miyabenol C), and tetramers (isohopheaphenol, ampelopsin H, and vaticanol C-like) (Mattivi et al. 2011; Vrhovsek et al. 2012; Chitarrini et al. 2017; Vezzulli et al. 2019). The predominant compounds were isohopeaphenol (up to 1300 mg/kg FW), miyabenol C isomers (up to 270 mg/kg FW), vaticanol C-like isomer and ampelopsin H (up to 226 mg/kg FW both), *Z*- and *E*-ω-viniferin (up to 127 mg/kg FW both), and α-viniferin (up to 120 mg/kg FW) (Table 12.1) (Vrhovsek et al. 2012).

12.4.2 Factors Modulating Stilbene Biosynthesis in Leaves

12.4.2.1 Genetic Factors

The genotype has been shown to be an important factor affecting the relative concentrations of various phenolic compounds in leaves. While few studies have analyzed the profiles of individual stilbenes, several authors have focused on total phenolic compound and flavonoid profiles.

The polyphenolic content in the leaves of eight *Vitis* genotypes (*V. candicans*, *V. riparia* cv *Gloire de Montpellier*, *V. rupestris* cv *du Lot*, *V. berlandieri*, *Börner* (*V. riparia x V. cinerea*), *V. coignetiae*, *V. amurensis*, and *V. vinifera* subsp. *sylvestris*) has been studied. The total polyphenol content ranged from 60.2 to 165.9 g/kg DW in blades and from 28.6 to 130.1 g/kg in veins. More specifically, the concentration of flavonol glycosides, the most abundant phenolic compounds in leaves, ranged from 3.6 to 20.6 g/kg DW in blades and from 0.8 to 7.7 g/kg DW in veins. From all the *Vitis* studied, *V. amurensis* stood out due to its high polyphenol content, particularly with regard to vein flavonols and flavanonols, while *V. vinifera sylvestris* displayed the widest flavonol profile diversification (Kedrina-Okutan et al. 2019).

In an earlier study, the same authors characterized the phenolic composition of the healthy leaves (separating blades and veins) of several *V. vinifera* varieties (Nebbiolo, Barbera, Pinot Noir, Cabernet Sauvignon, Grenache, and Shiraz) during the season (Kedrina-Okutan et al. 2018). Quantitative and qualitative differences were found between leaf sectors and among genotypes. Nebbiolo and to a lesser extent Pinot Noir displayed the highest flavanonol concentrations and, in the case of Nebbiolo, also the widest profile complexity.

Other authors have studied the phenolic profiles and antioxidant capacities of 20 white and red Portuguese varieties of *V. vinifera* leaves (Fernandes et al. 2013). They established that, in general, red varieties exhibited more often a higher concentration of phenolic compounds than white varieties. Tinto Cao, a red variety, and Côdega, a white, presented the highest polyphenol content. The following six polyphenols were quantified in this study: *E*-caffeoyltartaric acid, *E*-coumaroyltartaric acid, myricetin-3-*O*-glucoside, quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, and kaempferol-3-*O*-glucoside. Moreover, no relationship was found between phenolic composition and antioxidant activity.

Pantelić et al. (2017) characterized 22 grapevine leaves of diverse varietal origin cultivated in Serbia. In this study, ellagic acid and rutin were the most abundant compounds, found in concentrations up to 770 mg/kg and 450 mg/kg DW, respectively (Pantelić et al. 2017). The total phenolic content was in the range of 27.5–76.0 g GAE/kg DW.

12.4.2.2 Environmental Factors

Environmental factors also have a key role in the polyphenolic profile and amount in grapevine leaves.

Different light exposures of the grapevine has demonstrated that shading decreases the flavonoid content of the leaves, which is consistent with the role that these molecules play in protecting tissues from UV light. The authors of one study described the effect of different sun conditions (in sun-acclimated and half-shaded leaves) under field experiments in three varieties (Kocsis et al. 2015). They observed that the accumulation of quercetin-glucoside, kaempferol-glucoside, and quercetin-galactoside was more prominent in leaves exposed to full sunlight. Moreover, hydroxycinnamate *E*-caftaric acid accumulated significantly due to full sunlight.

Flavonoids are also produced upon UV-B radiation as an adaptive procedure in plants to reduce UV-B damage, and a correlation has been observed between physiological performance and quercetin-3-*O*-glucoside and kaempferol-3-*O*-glucoside in leaves of UV-B stressed vines (Schoedl et al. 2012).

Furthermore, the biosynthesis of phenolics is sensitive to diurnal differences in temperature, although with different temporal patterns. Indeed, a decrease in flavonoid biosynthesis has been observed when the temperature is limiting or excessive (Bavaresco et al. 2012).

The effects of drought stress on grapevine and grape quality have been investigated. Abiotic types of stress affect the primary and secondary metabolism of plants, having an impact on the content of carbohydrates and secondary metabolites such as polyphenols. Water deficit has been reported to upregulate the expression of genes of the anthocyanin pathway and to increase the levels of most polyphenols in the leaves, in particular *Z*-resveratrol-3-*O*-glucoside, kaempferol-3-*O*-glucoside, and quercetin-3-*O*-glucoside (Griesser et al. 2015). Moreover, a significant increase in proline in grapevine leaves under water-deficit conditions has been observed, suggesting this amino acid participates in the protection against the formation of excessive ROS (Doupis et al. 2011).

The composition and content of polyphenols in grapevine leaves according to their age and insertion level have been also reported. The compounds *Z*- and *E*-resveratrol-3-*O*-glucoside, catechin, quercetin-3-*O*-glucoside, caftaric acid, and quercetin-3-*O*-glucuronide are key markers of the age of grapevine leaves. For example, *Z*-resveratrol-3-*O*-glucoside and catechin are present in significantly higher levels in basipetal leaves, whereas semi-petal leaves contain significantly less quercetin-3-*O*-glucoside. However, highest concentrations of quercetin-3-*O*-glucuronide can be found in acropetal leaves (Schoedl et al. 2012).

A recent metabolomic study described the differences among grapevine leaves from several vegetative stages, growing localities, farming systems, and grapevine varieties using ultra-high performance liquid chromatography coupled with high resolution mass spectrometry (UHPLC–HRMS/MS) (Stranska et al. 2021). The samples were characterized in terms of fatty acids, fatty phenols, (lyso)-phospholipids, flavonoids, and organic acids, among other compounds. The authors

concluded that the harvesting season of the biomass explained most of the variability between the samples as the biochemical changes in *V. vinifera* metabolome during the inter-annual vegetation periods were substantial, followed by the growing locality and farming system used.

12.4.2.3 External Factors (Human Management)

A recent work investigated the influence of a mechanical stress on the stilbene content in grapevine leaves (Chitarrini et al. 2017). Mechanical wounding was performed on freshly cut leaves with cuttings of two sizes of leaf discs (1.1 and 2.8 cm in diameter), and the phenol content was monitored at 0, 6, 12, 24, 48, 96, and 120 h post cutting. The findings showed an accumulation of stilbenoid molecules such as *E*-resveratrol, *E*-piceid, miyabenol C, ampelopsin D, and quadrangularin A (Chitarrini et al. 2017). As previously demonstrated with grapevine cane, the different-sized discs caused a different response to the tissue, with a higher accumulation in the one with a 1.1 cm diameter. Aiming to produce stilbene-enriched extracts, the use of mechanical wounding could enable stilbene production in grapevine leaves to be stimulated and maximum levels to be reached.

12.4.3 Application of Leaves Biomass in Agri-Food Industry

12.4.3.1 Food

Grapevine leaves are characterized by a pleasing flavor and can therefore be used as a fresh boiled or baked food. Fresh, canned, or stuffed vine leaves have been consumed for a very long time, mainly in Turkish, Balkan, Greek, and Middle Eastern cuisines. For them to be edible, they have to undergo culinary treatments such as blanching, boiling, or steaming. For example, Sarma, grapevine leaves rolled around vegetables and minced meat, is one of the most popular dishes in the southeast of Europe and the Middle East (Lima et al. 2017).

12.4.3.2 Medicine

The most important and extended application of grapevine leaves extract is based on their bioactivity, mainly due to their phenolic composition. Since ancient times, *V. vinifera* leaves have been used in medicine due to various biological activities including hepatoprotective, spasmolytic, hypoglycemic, and vasorelaxant effects, as well as antibacterial, antifungal, anti-inflammatory, antinociceptive, antiviral, and particularly antioxidant properties (Pintać et al. 2019). The same authors developed a

neuroprotective assay with grapevine leaf extracts and described low anti-AChE activity shown by grapevine leaf extracts.

Moreover, the effect of leaf extracts on reducing lipid and protein damage and altering antioxidant enzymes status in the cerebral cortex, hippocampus, and cerebellum of Wistar rats has been investigated (Dani et al. 2010). The data obtained showed that grape leaf extracts present an important antioxidant activity in the brain tissues of rats. The authors suggested that the use of grape leaves could be important to retard or prevent the development of diseases associated with oxidative stress, such as the neurodegenerative diseases.

The antidiabetic effect of an aqueous grapevine leaf extract was tested on diabetic rats. One of the extract fractions (rich in polyphenolics) showed significant antihyperglycemic and antioxidant activity equipotent with the reference hypoglycemic agent (tolbutamide), which suggests that grapevine leaves could be a safe alternative medicine for controlling the blood sugar level of diabetic patients (Orhan et al. 2006).

A recent study demonstrated that the autochthonous Tunisian vineyard leaves showed a protective effect against experimental gastric ulcer. This gastroprotection seems to be related, at least in part, to antioxidant potential and also to anti-secretory acid effects. Thus, the grapevine leaves especially of wild varieties might act as a promising natural antioxidant substitute to synthetic molecules antioxidants, in addition to as a powerful natural anti-ulcer agent similar to synthetic drugs such as omeprazole, and thereby improve human health (Saadaoui et al. 2020).

Moreover, a work conducted in the region of Tlemcen, Sidi BelcAbbes, and Aflou (Algeria) showed an interesting antibacterial activity of methanolic grapevine extracts against bacteria such as *E. coli*, *Proteus mirabilis*, and *Bacillus cereus* and no activity against *Candida albicans* and *Aspergillus brasilicus* (Selka et al. 2016). The authors highlighted the importance of polyphenols in the leaves of *V. vinifera* and the possibility of using their extracts in a stable pharmaceutical form with important antibacterial proprieties, opening up the prospect of other formulations and many pharmaceutical and medical applications. Other authors have supported the above results with aqueous extracts of *V. vinifera* leaves (Orhan et al. 2009). They described more pronounced antibacterial activity against gram-positive bacteria (*S. aureus* and *E. faecalis*) than against gram-negative bacteria (*E. coli* and *P. aeruginosa*). Finally, juice from leaves has been also recommended as an antiseptic for eyewash (Fernandes et al. 2013).In one way or another, all the bioactivities presented by grapevine leaves are, at least partially, related with their antioxidant activities. In this line, the use of grapevine leaf extracts to produce dietary ingredients or in the formulation of dietary antioxidant supplements has been researched (Monagas et al. 2006). Both ingredients and supplements showed high antioxidant activity measured by the ORAC method.

The main applications of grapevine stems are resumed in Table 12.4.

Table 12.4 Main applications of grapevine leaf extracts

Leaf extracts	
Food	Medicine
– Pleasing flavor – Fresh, boiled, baked	– Antioxidant – Neuroprotective – Antidiabetic – Gastroprotective – Antimicrobial
Lima et al. (2017)	Monagas et al. (2006), Orhan et al. (2006, 2009), Dani et al. (2010), Fernandes et al. (2013), Selka et al. (2016), Pintać et al. (2019) and Saadaoui et al. (2020)

12.5 Vine Wastes: Trunk

In general, the term grapevine trunk encompasses the aerial parts of the vine, corresponding to the vine scion, which consists of the head, arms, and upper part of the scion/rootstock union (Fig. 12.2) (Hellman 2003). The trunk is a perennial organ that is never pruned and can be conserved for several decades and even a century. It can therefore be compared to a tree trunk. Due to the methods of propagation and culture of the vine, the trunk has the particularity of being composed of two genetically different individuals. Two different species of vines are grafted together, the rootstock providing its resistance to phylloxera and its vigor, and the graft providing its organoleptic properties (Tedesco et al. 2022). These materials could be considered to be vine waste when they are obtained during the uprooting for the vineyard's renewal due to the grapevine age, or when wood diseases lead the wine growers to tear up their plots. In the last decade, by reducing the surface of its vineyards by 13,500 ha/year, France has generated an important wood/trunk biomass, which is estimated to weigh more than 400,000 tons (FranceAgrimer 2016).

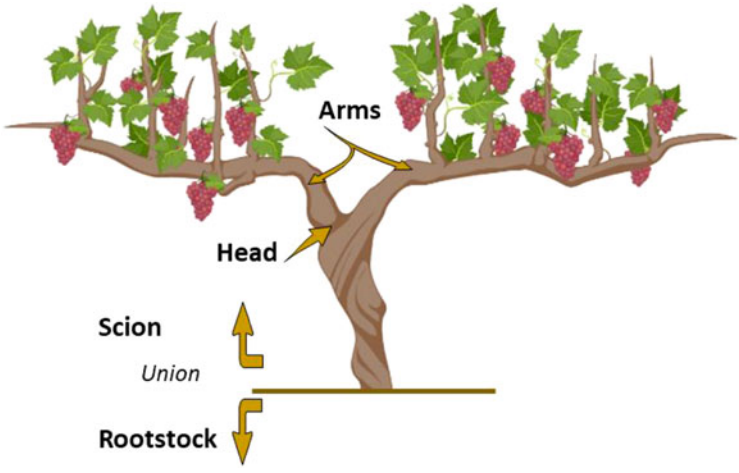


Fig. 12.2 A grafted vine is composed of a scion and a rootstock connected at the grafting area

12.5.1 Stilbene Composition in Grapevine Trunks

Currently, the literature agrees that *E*-ε-viniferin is the predominant compound in grapevine wood, with contents between 0.1 and 7.7 g/kg of wood (Martin et al. 2009; Amalfitano et al. 2011; Lambert et al. 2012; Gabaston et al. 2019). The next most predominant compounds are the tetramers isohopeaphenol and r-viniferin, with concentrations between 0.2–4.8 g/kg DW and 0.6–3.3 g/kg DW, respectively, as well as the trimer α-viniferin with a concentration of 4.7 g/kg of wood (Amalfitano et al. 2011; Gabaston et al. 2019). Resveratrol was also present in notable amounts, reaching 0.6–3.6 g/kg DW. In addition, the stilbenes reported to be present in lower concentrations are hopeaphenol (0.4–2.3 g/kg DW), ampelopsin A (0.4–2.2 g/kg DW), viniferol E (0.1–1.5 g/kg DW), or *E*-ω-viniferin (0.1–1.4 g/kg DW) (Amalfitano et al. 2011; Gabaston et al. 2019). More minor stilbenes are also present such as pallidol, leachianol G, *E*-piceid, miyabenol C, or *E*-astringin (Table 12.1). The total stilbenes content could reach up to 19.8 g/kg DW (Amalfitano et al. 2011; Rusjan et al. 2017; Gabaston et al. 2019).

Regarding the stilbene composition, it has been shown that the upper parts of the trunk and the graft interface (scion parts) are richer in dimers than the lower parts (rootstock parts), which contain more tetramers and fewer monomers. Indeed, it was shown that resveratrol dimers were mainly present in upper trunk parts such as the arm, the upper trunk, and the graft zone, with proportions of 44, 45, and 44% of total stilbenes, respectively (Gabaston et al. 2019). Furthermore, a recent study reported that the amount of stilbenes could vary along the trunk, as *E*-ε-viniferin was present in the arms in amounts between 2.2 and 6.2 g/kg DW, in the upper trunk between 2.0 and 5.0 g/kg DW, and in the graft zone between 2.3 and 7.7 g/kg DW (Gabaston et al. 2019).

12.5.2 Factors Modulating Stilbene Biosynthesis in Trunks

12.5.2.1 Genetic Factor

One of the most important factors influencing the stilbene composition of different grapevine parts is their genetic origin. Aiming to describe the metabolic events occurring during grafting and to identify markers of grafting success or failure, a study by Loupit et al. (2022) reported that European grapevine cultivars are richer in monomers and dimers, while American *Vitis* present higher levels of r-viniferin (Loupit et al. 2022). In fact, the study highlighted that the Merlot Noir cultivar in the homograft condition has the highest number of monomeric stilbenes in the upper part of the graft, whereas the homograft *V. berlandieri* x *V. riparia* cv Rességuier Selection Birolleau 1 (RSB1/RSB1) is the poorest in monomers (Loupit et al. 2022). *Z*-astringin is the predominant monomer in the upper grafting part of the Merlot/Merlot homograft (0.217 g/kg FW), whereas it represents only 0.0131 and 0.0149 g/

kg FW in the homograft RSB1/RSB1 and *V. berlandieri* x *V. rupestris* cv. 140 Ruggeri 33, respectively. On the contrary, the amounts of r-viniferin ranged between 0.13 and 0.18 g/kg FW in the wood of the homograft of American *Vitis*, whereas the Merlot/Merlot and Negrette33/Negrette33 homografts contained only 0.05 and 0.02 g/kg FW, respectively. Similarly, the content of the tetramer hopeaphenol reached 0.35 g/kg FW in the SO4/SO4 homograft, whereas only 0.14 and 0.19 g/kg FW were observed in the Merlot/Merlot and Negrette33/Negrette33 homografts (Loupit et al. 2022). Interestingly, in trunks of all European and American species, high concentrations of *E*-ε-viniferin are observed with variations from 0.6 g/kg FW in the Merlot/Merlot homograft up to more than 1 g/kg FW in Negrette, *V. berlandieri* x *V. riparia* cv. RSB1, and Selection Oppenheim 4 (SO4) homografts (Loupit et al. 2022). Globally, *E*-ε-viniferin is the predominant compound in the studied genotypes, and the differences observed between genotypes are mainly due to the levels of monomers and tetramers.

In addition to the direct aspect of the genetics of the cultivar or species, one of the factors influencing both the total amount of stilbenes and the proportions of different monomers and oligomers is the grafting process, in other words the influence that one genotype can have on the other. Few studies have analyzed the influence of the genotypes of one partner (scion or rootstock) on the stilbene content of the other grafting partner (scion or rootstock). Nevertheless, a recent study showed that the total stilbene level in the lower trunk of the 3309C rootstock was higher when it was grafted with Cabernet Franc as the scion (36.3 g/kg DW) than with Sauvignon Blanc (16.5 g/kg DW) or Gamay Noir (16.3 g/kg DW) (Gabaston et al. 2019). Similarly, it has been shown that some grafting combinations influence the quantity of hopeaphenol in the wood of the 140 Ru rootstock. Indeed, 0.1708 g/kg FW was found in the 140Ru/140Ru homograft and 0.1234 g/kg FW in the combination with Negrette, whereas only 0.0714 and 0.0919 g/kg FW were found in the combinations with Ugni blanc and Merlot Noir, respectively (Loupit et al. 2022). In this sense, the genetic inheritance of the scion could influence the stilbene profile in grapevine trunks. Besides, the rootstock origin can also modulate the level of stilbenes in the graft since more resveratrol was found in Merlot trunk when grafted with 140 Ru and SO4 (0.0515 and 0.0506 g/kg FW, respectively) than with RSB1 (0.0281 g/kg FW) (Loupit et al. 2022).

In order to produce extracts from harvested grapevine trunks, the influence of genetics on their stilbene content must be carefully considered as the cultivar or species can greatly influence the content of the final extract.

12.5.2.2 Environmental Factors

In addition to genetic factors, it is important to consider the effect age or climatic conditions on the stilbene content in grapevine trunks. A recent work analyzed three grafting combinations using 3309C as the rootstock that were planted between 1946 and 1977 (Gabaston et al. 2019). In this case, the oldest plant (Cabernet Franc/3309C) was found to contain the most stilbenes, suggesting an age effect. However,

there were no marked differences between Gamay Noir and Sauvignon Blanc grafted with 3309C even though they were planted 9 years apart. Moreover, the study showed strong differences between the combinations including Gravesac as rootstock even though they were planted only 3 years apart (Gabaston et al. 2019). In this sense, the influence of age on the stilbene content in the trunks should be minimal. This hypothesis seemed to be confirmed by the work of Loupit et al. (2022), in which all the combinations analyzed were less than 1-year-old and grown under controlled conditions in the same location, but showed variations in the stilbene content in the grapevine trunks (Loupit et al. 2022).

Biotic factors are also important modulators of stilbene content in grapevine trunk. In fact, different disease pathogens such as the so-called "esca proper" syndrome or Petri disease are able to induce an increase in total phenolics and especially stilbenes content at the site of infection, and/or at the healthy tissues next to the necrotic ones (Martin et al. 2009; Amalfitano et al. 2011; Rusjan et al. 2017). Although the stilbene profiles were similar qualitatively, a 2.5-fold increase in total stilbenes was observed in brown rotted wood of *V. vinifera* cv. Sangiovese infected by a complex of *Phaeomoniella chlamydospora*, *Phaeoacremonium aleophilum*, and *Fomitiporia mediterranea*. The highest increase observed in infected trunks concerns *E*-ε-viniferin, *E*-resveratrol, and glucoside derivatives. However, these results have to be requalified since Magnin-Robert et al. (2016) found no significant increase in stilbene content in esca-infected or apoplexy affected vines despite the increase in total polyphenol content in Chardonnay/41B (Magnin-Robert et al. 2016). Nevertheless, they observed an increase in total polyphenols and a slight stimulation of *STS* gene expression in the affected trunk, but no significant change in the transcription profile for the *PAL* gene (Magnin-Robert et al. 2016).The authors suggest that the observed accumulation of polyphenols cannot be explained by the accumulation of stilbenes, but rather by other polyphenols such as flavonoids. Recently, studying 1-year-old wood infected by *Neofusicoccum parvum*, Labois et al. (2020) found an increase in several stilbenes after 3 days (Labois et al. 2020). This increase concerned, in order of magnitude, α-viniferin, miyabenol C, ampelopsin C, restrytisol A, and pallidol. Minor increases were observed in *E*-δ-viniferin, *E*-resveratrol, and several unidentified resveratrol dimers (Labois et al. 2020). Similar results were observed 7 days after the infection, except for *E*-resveratrol and *E*-piceatannol, whose levels decreased. The relatively high content of resveratrol oligomers long after the infection compared with the decrease in *E*-resveratrol and *E*-piceatannol suggest that these monomers are used to form oligomers (Labois et al. 2020).

Finally, regardless of whether stilbenes are synthesized by the host or by a host-pathogen interaction, it appears that differences in tolerance to wood pathogens are related to the increase in stilbene levels in wood (Lambert et al. 2012; Magnin-Robert et al. 2016). Recently, Khattab et al. (2021) supported this idea by showing a genotype-dependent effect of infection by wood pathogens (Khattab et al. 2021). The authors studied different genotypes belonging to *V. vinifera* ssp. *sylvestris* varieties from Germany for their resistance to *N. parvum*. They studied the type of stilbenes synthesized in the wood of these genotypes and determined two

chemotypes, those producing glycosylated derivatives of resveratrol (piceid chemotype) and those producing oligomerized derivatives such as viniferin (viniferin chemotype). They highlighted that the most resistant individuals belong to the viniferin rather than the piceid chemotype and that individuals of the first group produce about 2 to 3 times more of these stilbenes and more rapidly. Moreover, the authors noted for one genotype in particular (*V. vinifera* ssp. *sylvestris* Ke15) a significant increase in *E*-ε-viniferin 2 days after inoculation and an increase in *Z*- and *E*-δ-viniferin after 3 days (Khattab et al. 2021). These data correlate with the induction of *STS*, mainly at the infection site. Thus, it is clear that some grapevine varieties, especially wild species, are able to react to wood pathogen infection and to protect themselves, albeit only partially. However, even though the authors reported an increase in most of the identified stilbenes, it is not clear today if it is the host that stimulates its own stilbene synthesis pathways, or whether it could be the reactional environment at the site of infection that provides adequate conditions for oligomer synthesis and the enzymatic arsenal of the pathogen (Amalfitano et al. 2011).

To sum up, the stilbene content in grapevine trunk seems to depend to a great extent on genetic inheritance, but could also be strongly modulated by biotic stress, in particular by wood pathogens belonging to the *Botryosphaeria* family. While further studies are needed, the influence of age and terroir on the stilbene amount seems to be minimal.

12.5.3 Application of Trunk Biomass in Agri-Food Industry

12.5.3.1 Agriculture

Owing to it richness in complex stilbenes (dimers, trimers, and tetramers), known for their powerful biological activities, grapevine trunk extracts have been studied against grapevine diseases, mainly against the grapevine downy mildew *P. viticola*. Gabaston et al. (2017) compared the effect of extracts of various woody parts of grapevines (cane, trunk, and roots) from a Cabernet franc and Tannat graft on the development of *P. viticola* (Gabaston et al. 2017). The trunk extract was particularly effective and was able to inhibit totally in vitro the sporulation of the pathogen at a concentration of 500 mg/L, which was more effective than the grapevine cane extract (800 mg/L). Moreover, the trunk extract had the lowest IC_{50} of the three extracts evaluated (76 mg/L). In order to understand the activity of these extracts, the authors tested the pure compounds and showed the high activity of the tetramers (r2-viniferin, r-viniferin, hopeaphenol) compared to the other stilbenes, with IC_{50} values ranging between 10 and 18 mg/L.

Recently, Taillis et al. (2022) demonstrated the high efficacy in vitro of an extract produced from a mixture of trunk and roots (70/30; w/w) against *P. viticola* (Taillis et al. 2022). Rich in tetramers, including r-viniferin, hopeaphenol, and isohopeaphenol (73.7, 63.6 and 47.0 mg/g of DW extract, respectively), this extract showed an IC_{50} of 70 mg/L against downy mildew sporulation, a value in agreement

with the previous work by Gabaston et al. (2017). Interestingly, as mobility is a primary factor in the mode of contamination of *P. viticola*, this extract was able to reduce or even completely inhibit the mobility of downy mildew zoospores at 25 mg/L (Gessler et al. 2011). The zoospores lost their integrity in contact with the stilbene extract, similar to what was observed by other authors on *B. cinerea* conidia (Adrian and Jeandet 2012). The authors pointed out that zoospores treated with the stilbene extract were also inhibited in their ability to infect new leaves. In addition, leaves treated with trunk and root extract induced the expression of grapevine defense genes such as *PAL* or *PR3*, which were correlated with an induced resistance against *P. viticola* (Taillis et al. 2022). Furthermore, greenhouse assays were performed using the grapevine trunk extract against grapevine downy mildew. Trunk extract was found to be able to reduce the severity of the disease by up to 40% at 300 mg/L. The authors also expressed their interest in developing a formulation to improve the efficiency of natural extracts.

The effect of trunk extract on the development of downy mildew infecting various cultivated plants such as potato (*Solanum tuberosum*), tomato (*Solanum lycopersicum*), and melon (*Cucumis melo*) has recently come to light (Taillis et al. 2022).

Apart from anti-mildew activity, Lambert et al. (2012) showed that oligomeric stilbenes in grapevine trunk such as *E*-ε-viniferin, hopeaphenol, isohopeaphneol, r-viniferin, and r2-viniferin also possessed antifungal activities against major wood decay fungi (Lambert et al. 2012). The stilbenes greatly reduced the growth of several *Botryosphaeriaceae* strains such as *D. serata*, *N. parvum*, and *E. lata*. In addition, the study by Khattab et al. (2021) showed that stilbenes synthesized in wood in response to infection in resistant varieties, and in particular viniferin-like oligomers, appear to play a direct role in inhibiting the growth and development of *N. parvum* (Khattab et al. 2021).

Overall, thanks to their stilbene content, grapevine wood extracts are of particular interest to researchers, especially in the agricultural field, with the aim of using them as a sustainable alternative to phytosanitary treatments. To our knowledge, the biological activity of grapevine trunk extracts has not been demonstrated in other fields of research such as human health or food chemistry.

The main application of grapevine trunk is resumed in Table 12.5.

Table 12.5 Main applications of grapevine trunk extracts

Trunk extracts
Agriculture
– Anti-oomycetes (grapevine and melon downy mildew, potato and tomato late blight) – Antifungal – Defense gene stimulator
Lambert et al. (2012), Gabaston et al. (2017), Khattab et al. 2021 and Taillis et al. 2022

12.6 Vine Wastes: Roots

12.6.1 Stilbene Composition in Grapevine Roots

In grapevine roots, the two main compounds are the *E*-ε-viniferin and r-viniferin. Nevertheless, a great variability has been reported, with a minimum value for *E*-ε-viniferin of 0.5 g/kg DW in the roots of *V. vinifera cv.* Gravesac (Gabaston et al. 2019), and a maximum of 18 g/kg DW, observed in the roots of the cultivar *V. vinifera* cv. Cabernet Sauvignon (Wei et al. 2016). Similarly, the r-viniferin content can vary from 3.0 to 24.3 g/kg of root (Esatbeyoglu et al. 2016; Gabaston et al. 2017, 2019) (Table 12.1).

Following the two main compounds, other oligomers reported to be predominant in grapevine root were the tetramers r2-viniferin, hopeaphenol, and isohopeaphenol and the dimer ampelopsin A. The average content of r2-viniferin was 3.7 g/kg DW, but it achieved levels of up to 7.0 g/kg DW (Gabaston et al. 2019). Esatbeyoglu et al. (2016) also found large amounts of r2-viniferin in a root extract (87.1 g/kg of extract), making it the second most important compound of their extract (Esatbeyoglu et al. 2016). Ampelopsin A, hopeaphenol, and isohopeaphenol showed respective average contents of 2.4, 2.1, and 1.4 g/kg DW, and maximum values up to 5.3, 6.9, and 4.6 g/kg DW, respectively (Gabaston et al. 2019) (Table 12.1). It should be noted that tetramers are the most represented stilbenes in underground parts of grapevines, with a relative abundance of 69.2 and 73.3% in roots and rootlets, respectively (Gabaston et al. 2019).

There is less *E*-resveratrol in the roots, with content oscillating between 0.1 and 2.6 g/kg DW (Németh et al. 2017; Gabaston et al. 2019). Furthermore, several stilbenes have been identified and shown to be present in minor to medium quantities depending on the study. These stilbenes include miyabenol C, viniferol E, *E*-piceid, pallidol, and piceatannol, which have been found at concentrations from 0.1 to 1.8 g/kg DW (Esatbeyoglu et al. 2016; Wei et al. 2016; Gabaston et al. 2019) (Table 12.1). Moreover, *E*-δ-viniferin was only quantified in the study by Wei et al. (2016), levels reaching less than 0.05 g/kg DW (Wei et al. 2016). Finally, some unusual stilbenes have also been found in roots, such as wilsonol C and heyneanol A from *V. vinifera* harvested in South Korea (Kim et al. 2014), or glucosylated derivatives of resveratrol (resveratroloside and resveratrol rutinoside) and *E*-ε-viniferin derivatives (*E*-ε-viniferin-diglucoside and *Z*-ε-viniferin-diglucoside), isolated from SO4 rootstock roots (Aja et al. 2019) (not included in Table 12.1).

12.6.2 Factors Modulating Stilbene Biosynthesis in Roots

12.6.2.1 Genetic Factor

As described above, there are large differences in stilbene content among the *Vitis* genotypes considered, and some of them are particularly rich in tetramers, such as

the roots of the Gravesac rootstock (grafted with Tannat) with up to 78.9% and the roots of the Fercal rootstock (grafted with Chardonnay) with 88.9% total stilbenes (Gabaston et al. 2019). In contrast, rootstocks like 4010 Castel or RGM show low levels of total stilbenes (average of 18.2 g/kg DW and 20.7 g/kg DW in root, respectively). Moreover, they possess the lowest amount of r-viniferin (6.3 and 9.3 g/kg DW; 4.5 and 4.9 g/kg DW in the roots and rootlets, respectively) (Gabaston et al. 2019).

As presented in the grapevine trunk, there is a significant influence of the scion on the stilbene content of the rootstock. As an example, the Gravesac rootstock showed a higher total stilbene content (43.1 g/kg DW) in the rootlets when grafted with Merlot compared to grafting with Tannat (23.3 g/kg DW) (Gabaston et al. 2019). The difference was characterized by inequivalent proportions of stilbene complexity. Indeed, more monomers were observed in Gravesac rootlets when grafted with Tannat (16% of the total stilbenes) than when they were grafted with Merlot (4.6% of the total stilbenes). On the contrary, more tetramers were observed in Gravesac rootlets when grafted with Merlot (76% of the total stilbenes; 32.7 g/kg DW) compared to Tannat (61% of the total stilbenes; 14.4 g/kg DW). More specifically, r-viniferin was the compound that showed pronounced differences, since the rootlets of Gravesac grafted with Merlot contained up to 23.9 g/kg DW of r-viniferin, whereas the level only reached 9.6 g/kg DW when grafted with Tannat. Similarly, the content of other stilbenes was influenced by the genetics of the scion in the grafting process such as the 3309C rootstock, whose content of hopeaphenol was much higher when grafted with Cabernet Franc (>5 g/kg DW) than with Gamay Noir (<2.3 g/kg DW) (Gabaston et al. 2019). Taking into account the influence of the scion on the stilbene content, and especially on the tetramer content, the choice of a possible material for the production of extracts enriched in stilbenes must be made with care, especially with regard to the grafting combination.

12.6.2.2 Environmental Factors

The evolution through the year of the content of resveratrol in roots of *V. amurensis* has been studied. An increase in the *E*-resveratrol concentration was observed from January to May (61.2–102.8 mg/kg DW), followed by a decrease in June and July (86.3 and 93.4 mg/kg DW, respectively), before another peak in the resveratrol concentration in September, with 123.4 mg/kg DW, this being the highest content measured during the year (Ji et al. 2014). The authors suggest that the differences in the microclimate and phytosanitary conditions in which grapevines grow may account for the observed variation in resveratrol content, since stilbenes are phytoalexins whose synthesis can be stimulated by external abiotic and biotic factors (Chong et al. 2009; Ji et al. 2014). During spring and summer, the amount of sunlight, and therefore UV, reaches its peak. This intensity could, among other factors, be at the heart of the increase observed in the resveratrol content. The stilbene-inducing effect of UV light is widely known in leaves, but a UV-C treatment

of vine seedlings (dug up) has been shown to lead to the induction of STS transcription in the roots in particular (Parage et al. 2012).

Additionally, the increase in the proportion of tetramers in grapevine root, particularly antimicrobial stilbenes such as r2-viniferin and r-viniferin, could be caused by the high pressure of microorganisms in the soil in contact with the roots, thus stimulating their production in the underground parts of the plant. Such a phenomenon was observed in wood infected by pathogens responsible for wood diseases (Martin et al. 2009; Amalfitano et al. 2011; Rusjan et al. 2017). In addition, it is likely that r-viniferin is produced by the oxidation of *E*-ε-viniferin, and the presence of metals such as copper, which is highly present in vineyard soils as a phytosanitary product, could also stimulated its synthesis (Velu et al. 2013; Keylor et al. 2015).

Moreover, certain environmental interactions such as the formation of mycorrhizae could lead to variations in the stilbene content in the roots. In fact, it was shown that a resveratrol tetramer (not identified by the authors) had a lower concentration in roots mycorrhized with *Rhizophagus irregularis* (Goddard et al. 2021). The authors suggest that the reduction in stilbenes may promote mycorrhization. In addition, a reduction in defense hormones was shown in mycorrhizal plants, which could explain the decrease in stilbenes.

12.6.2.3 External Factors (Human Management)

The production of stilbenes in the roots could also be modulated by exogenous chemical treatments. Indeed, a study focusing on hairy roots showed that MeJA-based treatments (100μM) on *V. vinifera* cv. Pinot Noir could stimulate a threefold increase in stilbene production compared with untreated ones after 10 days, stilbene levels reaching 1.13 mg/g FW (Tisserant et al. 2016). This was particularly the case when methyl-β-cyclodextrins were added to the medium. While the MeJA acted as an inducer of enzymes involved in the synthesis of phenolic compounds (Ruiz-García and Gómez-Plaza 2013), the effect of MCDs was due to the improved stilbene solubility. The authors showed that it is possible to reach stilbene concentrations in the culture medium of 249 mg/L, the main ones being arachidin-1 and arachidin-3. The effect of the treatments is most marked for δ-viniferin in roots and *E*-ε-viniferin in culture medium (Tisserant et al. 2016).

12.6.3 Application of Root Biomass in Agri-Food Industry

12.6.3.1 Agriculture

Root extracts represent a promising alternative for the control of vineyard diseases. Indeed, one study showed that a grapevine root extract was very effective at reducing the sporulation of *P. viticola* on a leaf disk assay with a total inhibition at 500 mg/L

(Gabaston et al. 2017). Interestingly, although this extract was less rich in total stilbenes (223 g/kg extract) compared to the cane extract (350 g/kg extract), it displayed an IC_{50} of 120 mg/L, whereas the cane extract was twofold less active (IC_{50} of 210 mg/L). The high relative activity was explained by the fact that the root extract was considerably richer in tetramers, which have the highest antimicrobial activities against *P. viticola* sporulation (i.e., IC_{50} of r-viniferin (12μM), hopeaphenol (18μM), and r2-viniferin (20μM)) (Gabaston et al. 2017).

In addition to the effect on cryptogamic vineyard diseases, root extract has demonstrated an interesting insecticide activity against a Solanaceae pest. Indeed, the development of *Leptinotarsa decemlineata*, known as the Colorado potato beetle, a major phytophagous pest of potato crops, has been affected at different levels by a root extract (Gabaston et al. 2018). The extract showed a convincing effect on the induction of chronic toxicity and the inhibition of larval development, and, less effectively, it inhibited food intake. Some authors suggest that stilbenes could act on the molting process of the target insects (Shimizu et al. 2000), or on the induction of oxidative stress, thus inhibiting the insects' food intake (Sambangi and Rani 2016). Finally, it seems that root extracts that are rich in various stilbenes are more effective due to the synergistic action of these stilbenes, as shown by Pavela et al. (2017).

12.6.3.2 Medicine

As stilbenes are known to be beneficial to human health thanks to their antioxidant, anti-tumor, and anti-obesity activities, some studies have focused on the use of stilbene-rich grapevine root extracts in the field of human health.

An extract of *V. thunbergii* var. *taiwaniana* roots made following a hot water extraction technique showed capacities to reduce in vitro lipid accumulation in 3 T3-L1 adipocyte cell lines with a strong reduction at a 500μg/mL concentration (Lu et al. 2017). It is interesting to note that the extract from grapevine stems or leaves did not present any activity in this study. Moreover, it was shown in vivo that the root extract, at a dose of 40 mg/kg of body weight for 5 weeks, led to a reduction in the weight of mice on a high-fat diet (Lu et al. 2017). In addition, an extract of *V. vinifera* roots harvested in South Korea also showed activity on pancreatic lipase (Kim et al. 2014). Reduced pancreatic lipase activity leads to a decrease in triglyceride absorption and could represent a tool to reduce obesity. The root extract significantly inhibited pancreatic lipase activity with an IC_{50} value of 19.6 mg/mL. The authors identified *E*-ε-viniferin as the main compound responsible for the activity of the extract (Kim et al. 2014).

Furthermore, stilbenes purified from a root extract (piceatannol, *E*-piceid, ε-viniferin, and δ-viniferin) showed strong antioxidant capabilities, in particular high hydroxyl radical scavenging activity with a scavenging rate greater than 50% for stilbenes at a concentration of 5μmol/L (Wei et al. 2016). Hydroxyl radical production in cells leads to a high cytotoxic effect, and therefore the authors hypothesized that stilbenes with high scavenging capacities were able to prevent

Table 12.6 Main applications of grapevine root extracts

Root extracts	
Agriculture	Medicine
– Anti-oomycetes (grapevine downy mildew) – Insecticide	– Anti-obesity (reduced lipid accumulation, inhibitor of pancreatic lipase) – Antioxidant (scavenger of hydroxyl radical nitric oxide) – Anti-inflammatory
Gabaston et al. (2017, 2018)	Kim et al. (2014), Esatbeyoglu et al. (2016), Wei et al. (2016) and Lu et al. (2017)

cell damage. Similarly, an ethanolic extract of *V. vinifera* roots enriched in *E*-ε-viniferin, r-viniferin, and r2-viniferin also showed free radical scavenging, antioxidant and cellular anti-inflammatory properties through DPPH, hydroxyl radical, and galvinoxyl radical scavenging assays (Esatbeyoglu et al. 2016). In addition, the root extract at 50μg/mL showed the capacity to protect cells from H_2O_2-induced DNA damage through antioxidant defense mechanisms, specifically the induction of HO-1- and γGCS-inducing activity, which is most likely due to Nrf2 activation. The extract also exerted antiatherogenic properties due to both free radical scavenging and the induction of antioxidant defense mechanisms (Esatbeyoglu et al. 2016).

The main applications of grapevine roots are resumed in Table 12.6.

From a global perspective, these studies show that grapevine roots could represent a particularly interesting raw material for the development of extracts with multiple biological activities with benefits for both plant and human health.

12.7 Conclusions and Perspectives

Ligneous *Vitis* waste (canes, stems, leaves, trunks, roots) represent a sustainable, available, and attractive biomass to value owing to its richness in stilbenes. Interestingly, the stilbenes composition widely varies owing to the nature of grapevine waste. Grapevine roots (total stilbenes >20 g/kg DW) were mainly constituted by tetramers, and trunks (total stilbenes >10 g/kg DW) were composed by dimers and tetramers, while grapevine canes (total stilbenes > 5 g/kg DW) contained principally monomers and dimers. Into a lesser extent, vine stems (total stilbenes 0.5–5 g/kg DW) were composed by monomers and dimers, while healthy leaves are mostly constituted by glycosylated monomers and contained more complex stilbenes after pathogen infection (total stilbenes 2–5 g/kg DW). The stilbene profile could nevertheless substantially fluctuate due to biotic, abiotic, or human external influence (Fig. 12.3). Genetics drastically influence the stilbene composition through the nature of the grape varieties or the scion/rootstock combination. In addition, due to its nature as phytoalexins, stilbenes tend to oligomerize to cope with various stresses, in particular during attack of pathogens. It is therefore important to strictly characterize the *Vitis* biomass before its potential value. Currently, the valorization of the grapevine cane is the most studied with reported applications in agriculture,

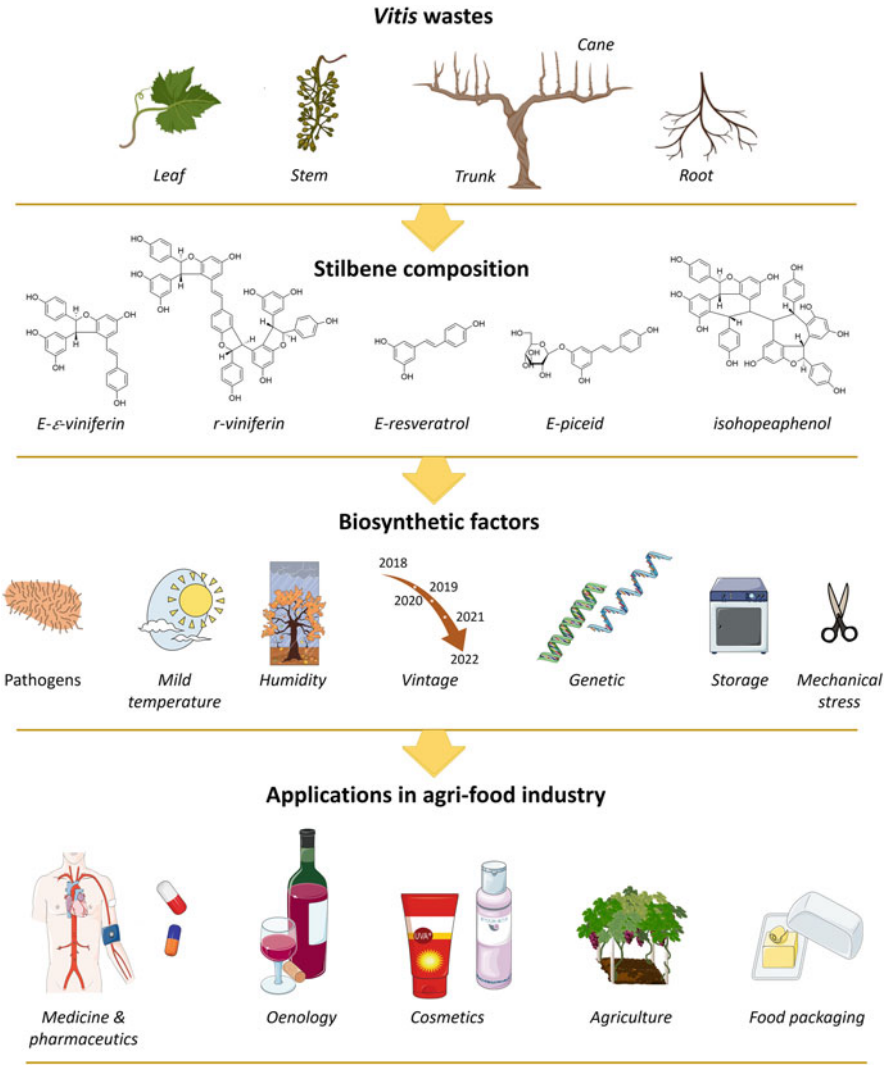


Fig. 12.3 Stilbene compounds present in grapevine wastes, factors affecting their biosynthesis, and major applications reviewed in the current work

medicine, foods, cosmetics, and oenology and in which commercial products are already available. Grapevine trunks and roots are mainly studied for their applications as natural oomycide, fungicide, and insecticide, while stems and leaves have several applications in medicine, oenology, and food (Fig. 12.3).

In conclusion, considering the potential commercial value of grapevine wastes, and the low cost and high abundance of these green mass byproducts, there is considerable interest in recovering and giving added-value to these waste, thus contributing at the same time to the circular bioeconomy.

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Chapter 13
Useful Bioactive Compounds from Olive Tree By-Products (Leaves, Branches, Fruits)

Marwa Abdallah, Rayen Ben Aoun, Marwa Ben Amor, Imen Touhami, Mariem Habibi, and Najla Trabelsi

Abstract Research of new bioactive compounds from natural raw materials, the by-products of the olive tree, attracts considerable attention due to their high potential as a source of useful molecules. The therapeutic virtues of olive tree by-products have been known since antiquity, it is mainly olive oil, and leaves are the most used in traditional medicine and recently in phytotherapy. The beneficial effects on human health of these two derivatives are multiple: antioxidants, hypoglycemic, antimicrobial, and anticancer. Although studies on the biological activities of other olive by-products (pruning wood, oil mill waste, and pomace) remain limited, these by-products are characterized by their richness in bioactive molecules. Indeed, studies have shown that the biological potentialities are related to the presence of monounsaturated fatty acids (especially oleic acid: C18:1) as well as other bioactive compounds such as tocopherols, carotenoids, phospholipids, and phenolic compounds (hydroxytyrosol, tyrosol, and oleuropein). Moreover, phytosterols are among the most interesting molecules of these coproducts that need to be studied in depth. This brief overview presents state of research on useful bioactive compounds from olive tree by-products.

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13.1 Introduction

Olive oil was considered as one of the most traditional agronomic products of Mediterranean region. In recent decades, the healthy properties of high-quality olive oil consumption explain the increase in olive cultivation worldwide. In 2018 and according to the Food and Agriculture Organization of the United Nations, 10.7 million hectares of olive trees was cultivated in 41 various countries, with a total production of 21.6 million tons of olives. This has resulted in the production of 3.2 million tons of olive oil, where Spain is the main producer (1.8 million tons) (Mar Contreras et al. 2020). During the production process, several bio-wastes were engendered, the most important of which were olive wood, leaves, pomace, stones, and olive mill wastewater. According to Rodrigues et al. (2015), 1 h of olive tree provides about 2500 kg of olives, being estimated that 100 kg of processed olives engenders 35 kg of olive pomace and 55–200 L of olive mill wastewater depending on the extraction process. Interestingly, leaf by-products generally represent around 5% of the olive's weight. These wastes pose several environmental problems when they are disposed in nature, owing to their high content of organic matter and phytotoxic compounds (Márquez et al. 2022). Despite this fact, its use is recently promoted because of its high nutrient content, especially biophenols, fatty acids, coloring pigments, tocopherols, phytosterols, and squalene content. In this perspective, a better valorization of these by-products, it is important to choose the suitable extraction technology and define their specific uses (Otero et al. 2021).

For this reason, those underutilized by-products could be regarded as an interesting resource with a large target market potential such as in pharmaceutical, cosmetic, and food industries. The main advantages are attributed to their specific molecular and biological properties, which confer them high antioxidant, anti-inflammatory, cardioprotective, and cancer preventive activities. Recovering their bioactive ingredients and converting them into value-added products in the food and dietary system promotes a sustainable processing method to supply nutritional products (Markhali et al. 2020). Several olive coproducts have been integrated in food, mainly in the bakery formulation as biscuits and bread. Regarding yoghurt formulations, different powders from olive leaf and olive mill wastewater (phenolic concentrate) have been tested in the preparation of functional dairy products without affecting the process of fermentation and probiotic number (Ribeiro et al. 2021). Thus, cosmetic application could be a new way to reuse these by-products. These biomolecules can serve as functional components in the formulation of cosmetics, enhancing the physical and structural characteristics of moisture, oil retention ability, emulsion and oxidation stability, viscosity, texture, sensory attributes, and shelf-life of the products. In fact, squalene has been reported to possess emollient proprieties, supporting the possibility of its utilization as an active ingredient in dermoprotective skin creams and other cosmetic formulations as a hydrating agent. In addition, oleuropein is

commonly cited as providing positive metabolic impact in skin care and antiaging benefits, as well as antiviral and antimicrobial actions (Rodrigues et al. 2015).

Therefore, the valorization of these coproducts has become a double necessity, ecological and economic. Indeed, it would allow to reduce many environmental issues and to contribute to the improvement of the profitability of the sector.

13.2 Biophenol Compounds

Biophenols or polyphenols constitute one of the largest groups of secondary plant metabolites. More than 8000 structures are known (Lima et al. 2016). They are found in different parts of the tree: seeds, flowers, leaves, stems, branches, and fruits of plants that are important for human diet.

Biophenols of olive biowastes are ubiquitous in plants, highly diversified, and mainly composed of phenolic alcohols and acids, flavonoids, secoiridoids, and lignans (Fig. 13.1).

Polyphenols are distinguished with more than one phenol group per molecule, along with other possible functional groups (Tapia-Quirós et al. 2022). They depend on the production and storage of the oil. Furthermore, the phenolic bioactive properties have demonstrated antiviral, antimicrobial, antioxidant,

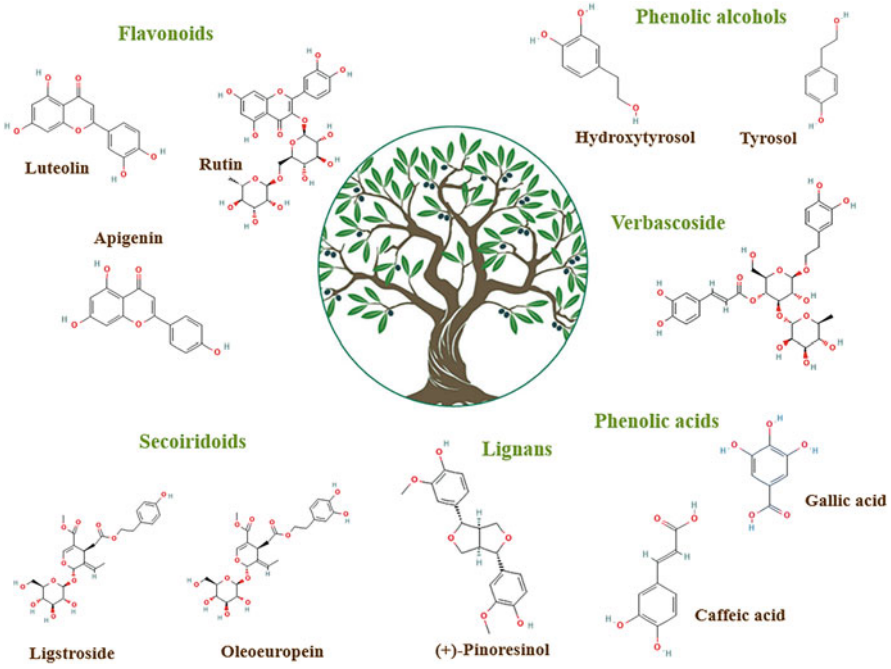


Fig. 13.1 The major biophenols described in olive by-products

anti-inflammatory, and anticarcinogenic activities (Özcan and Matthäus 2017; Otero et al. 2021) that represent high-value products with potential applications in the pharmaceutical, agricultural, cosmetic, and food industries (Dermeche et al. 2013; Caporaso et al. 2018; Gullón et al. 2020; Otero et al. 2021).

Several techniques have been employed to obtain phenolic compounds from olive by-products. Conventional extraction processes to recover phenols from olive by-products require the use of high-volume organic solvents and involve long extraction times. Additionally, the vulnerable compounds are susceptible to damage due to the high extraction temperature used (Cvjetko Bubalo et al. 2016). Various solvents, such as ethanol, methanol, acetone, and ethyl acetate by its own or its combination with water, have been employed to extract phenolic compounds from by-products (Gullón et al. 2018). Recently, the development and the usage of eco-friendly assisted methods have become progressively increasing as they enhance extraction efficiencies, decrease degradation of solute compounds at the same time, and ensure the high-quality and antioxidant capacity of the phenolic compound extracts in a shorter time with reduced energy. Several innovative extraction methods have been suggested, including ultrasonic, microwave, high hydrostatic pressure, and infrared-assisted extraction for phenolic compounds (Gullón et al. 2020). Moreover, the utilization of DES/NADES solvents (Chanioti et al. 2021; Da Rosa et al. 2021) and nonthermal technologies such as pulsed electric fields and high-voltage electric discharges, along with supercritical fluid extraction have been presented as interesting strategies for the efficient recovery of bioactive compounds from olive waste (Roselló-Soto et al. 2015; Žuntar 2019). Spectrophotometric methods have been used for the quantification of phenolic compounds from several natural sources. However, recently, other techniques have been employed, which can be classified into two main groups: firstly, the techniques of separation and detection, mainly chromatography coupled with different detectors, and secondly, the new techniques of structural analysis to characterize the structures of unknown molecules. Nuclear magnetic resonance (NMR), gas chromatography-mass spectrometry (GC-MS), and liquid chromatography-mass spectrometry (LC-MS) are the most widely used techniques (Emwas et al. 2019).

13.2.1 Phenolic Acids

Phenolic acids are phenol compounds containing a carboxylic acid. When this functional group is directly attached to the benzene ring, the compound is called hydroxybenzoic acid. When both the carboxylic acid functional group and the phenol ring are separated by two doubly bonded carbon atoms (a C=C bond), the phenolic compounds are called hydroxycinnamic acids (Al Mamari 2021). The biological activities of phenolic acids depend mostly on their bioavailability, which means the proportion of their absorption, digestion, and metabolism after entering the circulation system (Kumar and Goel 2019). Phenolic acids have attracted considerable attention in the fields of pharmaceutical and medicinal research as

they appear to play a role in the prevention of several human diseases (Al Jitan et al. 2018). Phenolic acids are an important group of valuable natural compounds that provide significant antiaging, antitumor, antimicrobial, and anti-inflammatory properties (Kiokias et al. 2020). The most prevalent phenolic acids available in olive by-products are verbascoside, caffeic acid, and gallic acid.

Gallic acid is a natural secondary metabolite commonly extracted from various natural matrixes. It represents a low-molecular-weight triphenolic compound with strong anti-inflammatory and antioxidant activities (Nouri et al. 2021). Gallic acid is recognized as a cardioprotective, neuroprotective, and anticancer agent. It is mainly due to their antioxidant properties against reactive oxygen species (ROS) signaling pathways (Kosuru et al. 2018). Gallic acid especially has been demonstrated in olive mill waste with an amount of 11.4–12.6 mg/kg (Cioffi et al. 2010), or 22.2–61 mg/kg (Russo et al. 2020).

Caffeic acid is frequently present in fruits, cereals, and food supplements used for human consumption in the form of simple esters with quinic acid or saccharides. Caffeic acid structure displays a phenolic ring with OH in positions 3 and 4 of the ring and a hydrocarbon chain in position 1 with an acid group (Alam et al. 2022). The features of caffeic acid chemical structure allow it to act as an effective metal reducing agent (Alam et al. 2022). It illustrates an extensive range of chemical and pharmacological activities. In addition, it is orally bioavailable for its anti-inflammatory, antioxidant, and anticancer bioactivities (Chen et al. 2018) as well as its immunomodulatory and neuroprotective activities (Sul et al. 2009). Caffeic acid has been shown in olive pomace with 6.7–13.5 mg/kg (Cioffi et al. 2010), or 19.2–57.3 mg/kg (Russo et al. 2020).

Verbascoside is a phenylethanoid glycoside originally isolated from mullein, but found in several other plant species. It is among the most widespread of the disaccharide caffeoyl esters (Alipieva et al. 2014). An important secondary metabolite is distributed in different plant species and shown to be a potent antioxidant with antiproliferative efficiencies and has exhibited anticancer activities against many cancers (Khalaf et al. 2021). Verbascoside has been usually reported in olive leaves, particularly in *Olea europaea* L. and almost in olive pomace. In olive leaves, this molecule has been found with an amount of 1000–2000 mg/kg (Luján et al. 2009). Nevertheless, in the olive pomace, verbascoside has been found at 10–20 mg/kg (Luján et al. 2009). They suggested that verbascoside is a powerful antioxidant biophenol extracted from olive mill waste that could be a promising compound with different interesting utilizations, specifically in cosmetic products or functional food (Cardinali et al. 2012).

13.2.2 Phenolic Alcohols

The phenolic alcohols are marked by the hydroxyl group, which is linked to an aromatic hydrocarbon group. The principal phenolic alcohols present in olive oils are hydroxytyrosol and tyrosol. These molecules are present at low concentrations in

fresh oils, which increase with stoking period because of secoiridoid hydrolysis (El Riachy et al. 2011). In addition, certain parameters significantly influence their concentration in olive oil, such as the stage of ripening, the geographical zone, and the oil extraction process (Malheiro et al. 2015).

Hydroxytyrosol (3,4-dihydroxyphenylethanol) has an antioxidant effect which not only depends on its capacity to remove oxidative chemical species, but also on its potential to boost the synthesis and activity of the antioxidant enzymes SOD, CAT, NOS, and glutathione reductase (GR) (Bertelli et al. 2020). The chemical formula of hydroxytyrosol is $C_8H_{10}O_3$, which is identical to tyrosol, except for an additional hydroxyl group in the meta-position in the aromatic ring. It is derived from the hydrolysis of oleuropein during maturation of olives (Santos et al. 2012). The content of hydroxytyrosol in olive oil, by contrast, depends on the type of olive tree and olive, the site of the plantation, the quality of the oil, and the process of elaboration of the olive oil (Robles-almazan et al. 2018). Due to its amphipathic character, it can be found in olive mill wastewater, pomace, and olive oil, on a free form (Robles-almazan et al. 2018). In view of its bioavailability, chemical properties, facility of formulation, and safety, hydroxytyrosol is considered as an attractive food supplement by the nutraceutical and food manufacturing industries (Bertelli et al. 2020). Moreover, hydroxytyrosols exhibit numerous health biological activities (Annunziata et al. 2021). In olive pomace, hydroxytyrosol has been shown as the main polyphenol found with a content of 83.6 mg/100 g (Antónia Nunes et al. 2018), 371 mg/L (Malapert et al. 2018), 24–25 mg/g (Madureira et al. 2020), and 13.3–31.0 mg/kg (Russo et al. 2020). However, in olive mill waste, hydroxytyrosol has been found with an amount of 483–1733.2 mg/kg (Mattonai et al. 2018), 1.52 g/L (Tundis et al. 2020), and 214 mg/kg (Russo et al. 2020). This compound was almost present in olive leaves with a percentage of 1.82% of hydroxytyrosol (Hayes et al. 2011).

Tyrosol (2-(4-hydroxyphenyl)-ethanol) is one of the major representative biophenols found in olives and oil where it occurs as it is or in the form of esters of the secoiridoid elenolic acid (Napolitano et al. 2010). Tyrosol has great pharmacological potential: antioxidant, anti-inflammatory, antiviral, and antitumor properties (Chandramohan and Pari 2016; Karkovi and Barbari 2019). Furthermore, it showed antigenotoxic activity and could prevent apoptosis in keratinocytes (Salucci et al. 2015). Tyrosol has been widely distributed in olive pomace and mostly in large quantities in oil mill waste with an amount of 1180–1560 mg/kg (Obied et al. 2005), 218.4–581 mg/kg (Mattonai et al. 2018), and 0.19–4.32 mg/mL (Bazoti et al. 2006). In olive pomace, tyrosol was represented with an amount of 96–124 mg/kg (Lozano-Sánchez et al. 2011), 69.6–196.7 mg/kg (Rubio-Senent et al. 2017), 34–71 mg/kg (Medina et al. 2018), and 20.7–21.6 mg/kg (Cioffi et al. 2010), while it is almost present in olive leaves with a content of 1.76% (Hayes et al. 2011).

13.2.3 Flavonoids

Flavonoids are very widespread plant secondary metabolites. They occur widely in nature and over 8000 molecules have been defined. Flavonoids tend to be largely planar molecules, with structural variation due partially to the pattern of modification by hydroxylation, methoxylation, prenylation, or glycosylation. Based on the degree of unsaturation and oxidation, flavonoids can be classified into several subclasses, such as flavones, flavonols, flavanones, and flavanols (Górniak et al. 2019). The most important flavonoids present in olive by-products are luteolin, apigenin, and rutin.

Luteolin is one of the most prevalent flavones that is naturally present in glycosylated form and can be found in various fruits and vegetables. Generally, it is available in plants, alone as an aglycone or bound to one or more sugars as a glycoside (Chae et al. 2019). A number of preclinical investigations indicate that luteolin displays a range of pharmacological actions, including antioxidant and reactive oxygen species (ROS) scavenging actions (Xu et al. 2019; Chen et al. 2020). Furthermore, luteolin exhibits antitumor and anti-inflammatory activities and induces apoptosis and cell death as well as the inhibition of migration and the invasion and the angiogenesis of cancer cells (Imran et al. 2019). An interesting antiviral effect has been recently suggested against the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) (Theoharides 2020). In olive leaves, luteolin-7-glucoside has been shown to be present in amounts of 5.05% (Hayes et al. 2011), 0.04% (Dekanski et al. 2009), and 127–191 mg/kg (Luján et al. 2009). Also, 4–14 mg/kg of luteolin 7-glucoside and 3–22 mg/kg of luteolin have been reported in olive pomace (Luján et al. 2009). Recently, Russo and co-workers have demonstrated the presence of 14.3–32.7 mg/kg of luteolin in olive pomace with a higher level of luteolin at a value of 2.5–36.2 mg/kg in olive mill wastewater (Russo et al. 2020).

Apigenin is largely distributed in plants such as vegetables, fruits, leaves, peas, and flowers and has been found to be the dominant type of flavonoid in celery, parsley, and chamomile (Škerget et al. 2005; McKay and Blumberg 2006; Yang et al. 2008). Apigenin has limited biodisponibility, but is more abundant than other common flavonoids, like quercetin and luteolin (Tang et al. 2017). Apigenin has attracted the interest of researchers owing to its low toxicity and numerous beneficial bioactivities. It has been shown as an anticancer agent in several experimental and biological studies. It induces cell growth arrest and apoptosis in different types of tumors (Abaza et al. 2007; Imran et al. 2020). The apigenin attenuates the cognitive decline and neuronal cell death associated with diabetes by suppressing ROS and nitric oxide synthase, as demonstrated in a diabetic rat model (Xiao-Yuan et al. 2015). The presence of apigenin-7-glucoside with a content of 137–260 mg/kg has been revealed (Luján et al. 2009). Similarly, apigenin 7-glucoside was found in a high concentration in seven of the main Tunisian varieties, Chemchali (2.62 g/kg), Chemlali (1.93 g/kg), Chetoui (2.36 g/kg), Gerboui (2.34 g/kg), Sayali (1.31 g/kg), Zalmati (2.68 g/kg), and Zarrazi (2.08 g/kg) (Abaza et al. 2007). In olive pomace, an

amount of 8–22 mg/kg of apigenin and 0.5–6.3 mg/kg of apigenin-7-glucoside has been detected (Luján et al. 2009). Lately, Russo et al. have suggested the presence of 11.4–13.6 mg/kg of apigenin in olive pomace and 2.5–6.5 mg/kg in oil mill wastewater (Russo et al. 2020).

Rutin is a flavonol found in various common plants such as apple and tea, which is also called vitamin P and quercetin-3-O-rutinoside (Kröner et al. 2012). Rutin is the principal glycosidic form (a 3-O-rhamnoglucoside) of quercetin that is the most abundant flavonol in vegetables and fruits. On the other hand, the presence of four hydroxyl groups and a rutinose molecule in the structure of rutin is considered to be responsible for its biological activities (Semwal et al. 2021). This molecule is a powerful compound that may be envisaged in the therapy of various diseases, in particular hepatotoxicity and gastrointestinal diseases and diabetes, and protects the organs from any free radical-producing agent. In addition, it is a major ingredient in several nutraceuticals and is one of the most therapeutically active compounds (Hosseinzadeh and Nassiri-Asl 2014; Semwal et al. 2021). Rutin is most prevalent in oil mill wastewater with a content of 440–640 mg/kg (Obied et al. 2005). However, in olive pomace it was found at 0.63–0.69 mg/kg (Lama-Muñoz et al. 2013) and 1.1–1.5 mg/kg (Russo et al. 2020).

13.2.4 Secoiridoids

Secoiridoids constitute a group of compounds which are typically linked by glycosidic bonds, generated from the secondary metabolism of terpenes. They are only available in the family Oleaceae, including *Olea europaea* L., and they are characterized by the presence of elenolic acid in its glycosidic or aglyconic form (Servili and Montedoro 2002). They may be derived from iridoids in plants, which are cleaved by redox enzymes and subsequently undergo several secondary changes (oxidation, epoxidation, esterification) of the hydroxyl groups generated in the main skeleton (Dinda et al. 2007). Oleuropein and ligstroside were recognized as the most important secoiridoids found in olive by-products.

Oleuropein is an ester of hydroxytyrosol containing an oleosidic skeleton and a carbohydrate group. Chemically, it comprises of three structural subunits: a secoiroid called elenolic acid; a polyphenol, namely, 4-(2-dyhdroxyethyl)benzene-1,2-diol that is called as hydroxytyrosol; and a glucose molecule (Omar 2010a). Oleuropein is most abundant during the first stage of fruit development, namely, the growth phase, and then gradually decreases as the development changes from the green to the black maturation phase (Imran et al. 2018). Oleuropein is distinguished by its strong efficacies against viruses, bacteria, yeasts, fungi, molds, and other parasites (Scognamiglio et al. 2012; Gálvez et al. 2014). Also, it has been reported to have antioxidant, anticancer, anti-inflammatory, and cardioprotective (Omar 2010b; Barbaro et al. 2014; Piroddi et al. 2017). The oleuropein has been shown as the most significant phenolic component of olive leaves. Oleuropein has been reported to be the highest phenolic compound in olive leaves, representing 9% of the

total leaf weight (dry matter) in olive leaves of the Greek cultivars koroneiki, megaritiki, and kalamon (Kiritsakis et al. 2010). Additionally, oleuropein has been shown with a quantity of 17,000–25,000 mg/kg (Luján et al. 2009) and a percentage of 19.8% (Dekanski et al. 2009), along with a percentage of 40.33% in another research (Hayes et al. 2011) and 56% of the phenolic fraction in the olive leaves of Spanish cultivars (Guinda et al. 2015). Similarly, oleuropein has been detected at significant concentrations in seven of the main Tunisian varieties, Chemchali (5.19 g/kg), Chemlali (2.41 g/kg), Chetoui (4.53 g/kg), Gerboui (2.38 g/kg), Sayali (1.68 g/kg), Zalmati (4.7 g/kg), and Zarrazi (4.06 g/kg) (Abaza et al. 2007). However, oleuropein has been reported in olive pomace and oil mill wastewater, but in less quantity than in olive leaves. In olive pomace, oleuropein has been shown in a quantity of 10–660 mg/kg (Luján et al. 2009), of 81.7–83 mg/kg of Cilento (Campania, Italy), and of 23.3–24 mg/kg of oleuropein aglycone (Cioffi et al. 2010). Moreover, 7.62–14.67 mg/kg of oleuropein has been demonstrated in olive oil waste called alperujo (Rubio-Senent et al. 2017). Similarly, the percentage of phenolic composition has been shown as 1.96% for oleside riboside, 1.65% for the oleuropein derivative (Antónia Nunes et al. 2018), and 1.3–11.0 mg/kg for oleuropein (Russo et al. 2020). In oil mill waste, they have been detected at 0.51 g/L of oleuropein by consecutive use of microfiltration, nanofiltration, and reverse osmosis (Tundis et al. 2020). Alternatively, one other study also demonstrated the occurrence of 5.7–27.0 mg/kg oleuropein (Russo et al. 2020).

Ligstroside (deacetoxy-ligstroside aglycon) is one of the phenolic compounds present in olive cultivars that contributes to the piquant odor of extra-virgin olive oil (Ghanbari et al. 2012). It differs from oleoside by a hydroxyl group. Ligstroside has been demonstrated higher in olive pomace compared to oil mill wastewater and olive leaves. It was shown with a quantity of 27.1–31.1 mg/kg of olive pomace from Italy (Cioffi et al. 2010), 15.7–17.3 mg/kg (Suárez et al. 2009), and 2.5–2.9 mg/kg (Russo et al. 2020). However, in the olive leaves, ligstroside has been found with an amount of 3.251–3.845 mg/kg (Talhaoui et al. 2014) and 0.0087–0.0092% in the oil mill wastewater (Dermeche et al. 2013).

13.2.5 Lignans

Lignans are widespread diphenolic compounds in the plant kingdom and produced by oxidative dimerization of 2 units of phenylpropane. Structures formed by dimerization between the two central carbon atoms (8 and 8′) of the side chains of the phenylpropanoid units (C6–C3) form a lignan, while other types of linkages are classified as neolignans (Markulin et al. 2019). It consists of two phenol units linked by four carbons. The two main bioactive lignans described are (+)-pinoresinol and (+)-1-acetoxypinoresinol (Otero et al. 2021). These lignans have numerous biological properties such as antioxidant, antitumor, antiviral, antibacterial, insecticidal, fungistatic, and antiparasitic activities (Markulin et al. 2019). Pinoresinol is the most common compound found in olive by-products.

Pinoresinol is a biphenolic lignan used for its therapeutic properties. Pinoresinol showed promising properties as a natural entity against oxidative stress, liver damage, and diabetes (Youssef et al. 2020). It exhibits antifungal activities and potential as a therapeutic agent for the treatment of infectious fungal diseases in humans (Hwang et al. 2010). Pinoresinol is almost absent in olive leaves with a quantity of 0.0033–0.0047 mg/kg (Cittan and Çelik 2018), but it is higher in olive mill waste, 2.6–3.2 mg/kg (Suárez et al. 2009) and 17–137 mg/kg (Medina et al. 2018).

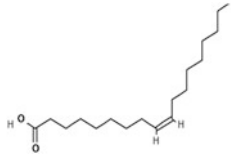
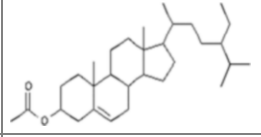
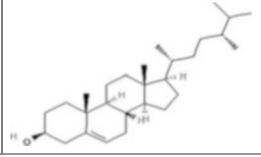
13.3 Triterpenoids

Terpenoids are a very important class of natural compounds produced by different plants. They have acquired an important interest since the antiquity, thanks to their wide range of therapeutic, cosmetic, and food applications. The olive oil (OO) is considered as a rich source of terpenoids (Jaeger and Cuny 2016) (Table 13.1).

According to literature, just 33% of triterpenoids are extracted during olive oil production, so around 67% of these compounds are present in the by-products. In fact, triterpenes correspond to 17.6, 1.5, and 0.8% of the bioactive composition of olive pomace (OP), olive seed (OS), and oil mill wastewater (OMWW), respectively. Among the triterpenoids (Table 13.1), squalene, maslinic, and oleanolic acids are the major compounds (de la Torre et al. 2020).

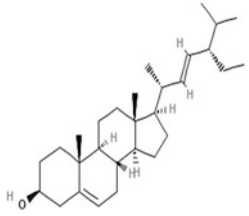
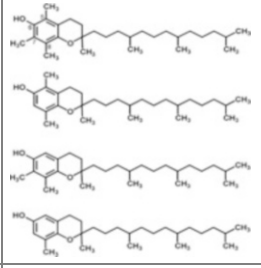
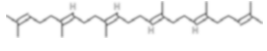
Squalene, a hydrocarbon chain ($C_{30}H_{50}$), is a triterpene containing six unsaturated bonds with an antioxidant nature. It is a very valuable compound; it represents an intermediate on phytosterols and cholesterol biochemist pathways and it is highly appreciated by its biological importance (Lozano-grande et al. 2018). This molecule was originally isolated from shark liver oil but now it seems interesting to find other renewable sources in order to conserve shark populations. In this regard, several studies have shown that a number of plant sources contain a considerable amount of squalene (Singh et al. 2019). Regarding OO by-products, squalene content reaches 300 mg/100 g DR in both olive pulp and OS, 25 mg/100 g DR in the case of OMWW (Maestri et al. 2019; Otero et al. 2021), and varies from 500 to 6000 mg/Kg in OP oil (Mateos et al. 2019). Squalene is an interesting bioactive substance that provides several benefits to skin tissue, including antioxidant properties at the dermal layer against solar radiation, thus serving as a biological screen for singlet oxygen (Micol et al. 2005). Furthermore, squalene can also function as a sink for highly lipophilic xenobiotics, favoring their removal from the body (Ghanbari et al. 2012). Regarding other remarkable characteristics of squalene, it has been reported to have emollient properties, which allows it to be utilized as an active ingredient in cosmetics and skin protection creams and other cosmetic formulations as a moisturizing or emollient agent (Stavroulias and Panayiotou 2005). In addition, squalene emulsions have been used for various formulations, especially for the delivery of vaccines, drugs, and other medicinal substances (Ghanbari et al. 2012). Squalene is highly orally absorbed and has been used to enhance the oral administration of therapeutic

Table 13.1 Chemical structure and content of different bioactive compounds in olive by-products

Group	Compounds and structure		Principal residue content (mg/100 g DR)				Ref.
			Olive pulp	Seeds	OMWW	Olive pomace	
Fatty acids	Oleic acid		2000	14,000	3000	–	Maestri et al. (2019) and Hannachi et al. (2020)
	Linoleic acid		350	4500	–	–	
Phytosterols	β-Sitosterol		200	200	–	–	Maestri et al. (2019) and Otero et al. (2021)
	Campesterol		80	12	–	–	

(continued)

Table 13.1 (continued)

Group	Compounds and structure		Principal residue content (mg/100 g DR)				Ref.
			Olive pulp	Seeds	OMWW	Olive pomace	
	Stigmasterol		100	6	–	–	
Tocopherols	α, β. γ, and δ		30	30	2	2.63	Aggoun et al. (2016), Fiedor and Burda (2014), Maestri et al. (2019), Montenegro et al. (2015) and Yanık (2017)
Triterpenoids	Squalene		300	300	25	5000–60,000	Maestri et al. (2019), Mateos et al. (2019) and Otero et al. (2021)

molecules. Today, some claim that squalene can provide improved quality of life if taken continuously and orally (Reddy and Couvreur 2009).

Traditional extraction methods, such as the Soxhlet method, are the most commonly used method as standard for the extraction of triterpenoids and the extract is considered to contain 100% of the extractable material. It usually uses organic solvents such as hexane, which is the most commonly used solvent for large-scale extractions due to its relatively low cost (Mercer and Armenta 2011). However, as this method is used at low pressure, the yield can be low, and the development of new techniques at higher pressures can help raise the output and reduce the processing time. In this case, ultrasonic extraction combined with organic extraction may lead to higher yields. Another method of separation is the complexation of silver ions which is based on the complexation reaction between Ag + and unsaturated carbon double bonds. This method is inexpensive, its operation is continuous, and it allows the recycling of reagents (Rosales-Garcia et al. 2017). Another promising technology to obtain squalene from the biological matrix is supercritical fluid extraction with CO2 as solvent. This technique was studied because of its advantages over conventional extraction. The extract in this case has better quality, has better biostability, and is easy to remove from the extracted matrix. Nevertheless, it is considered as an expensive technology (Kraujalis and Venskutonis 2013).

13.4 Phytosterols

Plant sterols, commonly known as phytosterols, are natural bioactive molecules representing some triterpene groups. Most phytosterols have a side chain composed of nine to ten carbon atoms (Ms et al. 2018). During the OO extraction, higher levels of phytosterols have been generally described in the solid waste (Mateos et al. 2019). According to the results compiled, these compounds are distributed as follows: about 10% of the total phytosterols are found in OO, whereas around ~80% are present in by-products. The total phytosterol content in olive pulp is around 380 mg/100 g DR (200, 80, and 100 mg/100 g DR for β-sitosterol, campesterol, and stigmasterol, respectively), while it is lower in OS, around 219 mg/100 g DR (200, 13, and 6 mg/100 g DR for the previously indicated compounds) (Maestri et al. 2019). According to the bioactive compounds present in these residues (Table 13.1), phytosterols correspond to an average of 8.9% and 2.7% of the bioactive composition of olive pulp and OS, respectively (Otero et al. 2021).

β-Sitosterol is considered as a bioactive phytosterol, with a chemical structure similar to the mammalian cell-derived cholesterol (Babu and Jayaraman 2020). It is considered as a safe and potential nutritional complement, with a long history of use as a pharmaceutical product, without harmful side effects. Many scientific reports recognized that it possesses antinociceptive, anxiolytic and sedative, analgesic, immunomodulatory, antimicrobial, anticancer, and anti-inflammatory protective effects on respiratory diseases in addition to wound healing effect and anti-diabetic activity (Abdou et al. 2019; Fraile et al. 2012; Babu and Jayaraman 2020). It also

displayed protective effects on digestive infections. It is well demonstrated that phytosterols have a significant positive influence on the decrease of serum cholesterol, as well as on the risk of heart disease in humans (Lin et al. 2010). They also have significant roles in pharmaceutical areas (production of therapeutic steroids), nutrition, and cosmetics. As a result, they are usually utilized in these industries as value-added additives (Ms et al. 2018). Currently, free phytosterols extracted from several plant sources are largely used in enriched foods and dietary supplements. Some commercial products such as margarine, yogurt, yogurt drinks, and orange juice contain plant sterols (Ms et al. 2018).

The extraction techniques (conventional or nonconventional techniques) for phytosterols are largely related to the nature of the matrix and the form of phytosterols (free, esterified, and glycosylated). The conventional methods include Soxhlet extraction, maceration, heating under reflux, percolation, and hydrodistillation. Among these techniques, Soxhlet and maceration methods have generally been the most used methods and still considered as a reference to the recently developed methods. However, the organic solvents used in these conventional extractions are harmful for human health as well as the environment (Smith 2003). They have other limitations such as a long time for extraction, the requirement of an extra pure solvent, the necessity of solvent evaporation, a lower selectivity of extraction, and thermal degradation of heat-sensitive compounds. For these reasons, the demand for new technologies has increased to limit the use of organic solvents and provide some advantages over conventional extraction techniques (Ms et al. 2018). Wide ranges of efficient and promising techniques have been introduced in the past decades to overcome these limitations. The most promising techniques for the extraction of bioactive compounds are microwave-assisted extraction (MAE), enzyme-assisted extraction (EAE), ultrasound-assisted extraction (UAE), pulsed electric field-assisted extraction (PEFAE), hydrotropic extraction (HE), pressurized liquid extraction (PLE), and supercritical fluid extraction (SFE). Among these techniques, PLE and SFE have been performed under pressurized conditions. SFE, PLE, EAE, and MAE have typically been used to extract sterols (Azmir et al. 2013; Brusotti et al. 2014).

13.5 Tocopherols

Olive biowastes are a rich source of several antioxidant compounds such as tocopherols (Table 13.1). Tocopherols, the major forms of vitamin E, are a group of fat-soluble biophenols. There are four different isoforms of tocopherols: α (alpha), β (beta), γ (gamma), and δ (delta) tocopherol.

Regarding their distribution, higher amounts were reported in olive by-products (77.5%) than in OO (22.8%). α-Tocopherol is the main form of vitamin E found in OP (2.63 mg/100 g DR). α-Tocopherol is considered as the most active form of vitamin E (Fiedor and Burda 2014; Montenegro et al. 2015). On the other hand, α-tocotrienol (0.1), γ-tocopherol (0.04), and β-tocopherol (0.03 mg/100 g DR) are

minor components of OO. In olive pulp and OS, this amount reaches about 30 mg/100 g DR, while a lower content is observed in OMWW, ~2 mg/100 g DR (Aggoun et al. 2016; Yanık 2017; Maestri et al. 2019).

Regarding their powerful antioxidant potential, tocopherols have been suggested to reduce the risk of cancer (Ju et al. 2010). Several research findings indicate that a poorer nutritional status of vitamin E is associated with an increased risk of certain types of cancers. For this reason, α-T has been the most commonly used form of tocopherols for cancer prevention studies (Das Gupta and Suh 2016). Notably, the functions of the respective tocopherols differ depending on their structure. For example, γ-tocopherol was effective for the inhibition of colon and lung cancer and for the control of cancer progression, while δ-tocopherol was greater than α-tocopherol and γ-tocopherol in tumor inhibition activity. In addition, α-tocopherol is also found to be a reflection of daily dietary status (Zhang et al. 2022). All tocopherols except β-tocopherol inhibit smooth muscle proliferation. However, they show important in vitro and in vivo anti-inflammatory potential and their molecular mechanisms of action involve, at least in part, the modulation of inflammatory factors responsible for the initiation of several phases of inflammation (Ahsan et al. 2014; Mathur et al. 2015). Moreover, they are known as the best natural antioxidants for lipids in foods and biological systems. Scientists, interested in antioxidant mechanisms, commonly believe that tocopherols, especially α-tocopherol, exert their protective actions by interrupting the autocatalytic reaction cycles by donation of their phenolic hydrogen to peroxyl radicals and by stabilization of preformed hydroperoxides (Kamal-Eldin and Budilarto 2015).

Several techniques have been described for extracting tocopherols. The extraction methods include those using solvent extraction (direct solvent extraction, Soxhlet extraction, and saponification), maceration (MAC), extraction with matrix solid-phase dispersion (MSPD), supercritical fluid extraction (SCFE), and ultrasonic-assisted extraction (UAE) (Wang and Weller 2006; Ramos 2012). Each of these extraction methods has certain advantages and inconveniences. Therefore, the selection of the extraction method will depend on the physicochemical characteristics of the sample (Saini and Keum 2016). Nevertheless, solvent extraction remains the most commonly used method for extracting tocols due to their hydrophobic nature. Among the solvent systems used, hexane remains the most frequently employed, but ethanol and solvent mixtures such as heptane-diethyl ether and ethyl acetate-hexane have also been used for their recovery (De Camargo et al. 2018).

13.6 Fatty Acids

Fatty acids (FA) are the primary constituent of fats and have an essential role in biological systems. Fatty acids can be as free or bound forms such as cholesterol and phospholipids. They consist of a hydrocarbon chain with a methyl end (CH_3) and a carboxyl end (COOH). Most often, the fatty acids that make up dietary fats contain 16–20 carbon atoms. This carbon chain can be deprived of any carbon-carbon

double bond, in which case the fatty acids are said to be saturated (SFA). It can also contain a double bond (monounsaturated fatty acid [MUFA]) or several double bonds (polyunsaturated fatty acid [PUFA]). For unsaturated fatty acids, they are often referenced according to the position of the first double bond in relation to the terminal methyl group (Guesnet et al. 2005). Olives are oil-rich, entirely composed of triglycerides with FAs, particularly oleic, palmitic, and linoleic acids (Table 13.1). The majority of FAs are extracted during the process of OO production (~80%); thus, their concentration is significantly lower in the olive by-products (~20%) (Alu'datt et al. 2017). The olive pulp contains about 10% of residual oil, rich in FAs, especially oleic and linoleic acids, with contents reaching up to 2000 and 350 mg per 100 g DR, respectively (Antónia Nunes et al. 2018). OS are considered a great source of unsaturated fats, with oleic and linoleic acids being the most abundant fats. According to recent studies, OS contain about 14,000 mg/100 g DR of oleic acid and 4500 mg/100 g DR of linoleic acid (Maestri et al. 2019; Hannachi et al. 2020). Finally, Antónia Nunes et al. (2018) reported that about 3000 mg/100 g DR of oleic acid was detected in OMWW, but devoid of linoleic acid. According to other works, a mixture of saturated (SFA), monounsaturated (MUFA), and polyunsaturated fatty acids (PUFA) constitutes the lipid fraction of the olive pomace. Thirteen fatty acids were detected at the composition of the OP oil. The oleic acid was the most abundant, with a percentage of 75% of the total fatty acids, followed by palmitic and stearic acids (10% and 3%, respectively) (Antónia Nunes et al. 2018).

Fatty acids have been reported to exert positive effects on reducing the risk of some kinds of cardiovascular and inflammatory diseases and maternal and infant nutrition (Finley and Shahidi 2001). The prospective cohort study PREDIMED (Primary Prevention of Cardiovascular Disease with a Mediterranean Diet) demonstrated that the consumption of MUFA was related with a lower risk of cardiovascular problems (Estruch et al. 2018), in addition to other positive effects like diabetes prevention (Salas-Salvado et al. 2018). For the past few decades, a lot of research on PUFAs has been conducted. Scientists have approved that the consumption of PUFAs also can help to prevent cardiovascular diseases. It significantly reduced the threat of death, as well as cardiovascular mortality (Kapoor et al. 2021). As well, recent reports suggest that these bioactive compounds have anticarcinogenic, antiobesity, and antidiabetic effects (Nagao and Yanagita 2005).

There are several techniques used for the extraction of fatty acids. Lipid extraction using only nonpolar solvents is a technique that has been widely used in the past for the extraction of lipids from different types of biomasses by Soxhlet extraction. Generally, nonpolar solvents such as hexane and ethyl ether are used for this purpose. Nevertheless, sometimes this method is found to be not very efficient. Therefore, an organic cosolvent system (mixture of polar and nonpolar solvents) is better suited for lipid extraction. Chloroform/methanol (1:2) and chloroform/methanol (2:1) mixtures are recognized cosolvents used for this purpose. Polar solvents improve and facilitate extraction (Deshmukh et al. 2019).

13.7 The Macromolecules

Compared to all other constituents, plant macromolecules exhibit a high molecular weight. It can be around 10,000 to more than 10,000,000, unlike other plant metabolites, which rarely exceed a molecular weight of 1000. Chemically, long chains of small structural units or "building blocks," bonded covalently in various ways, form macromolecules**.** Major plant cell walls are filled with various macromolecules (Fig. 13.2), such as cellulose, hemicelluloses, and lignin (Wang and Hong 2016).

13.7.1 Definition

13.7.1.1 Cellulose

Cellulose remains one of the most profuse biopolymers on Earth. It is widely found in nature, e.g., in trees, agricultural crops, and other plant biomass (Li et al. 2021). The olive tree actually has a higher cellulose content of 32% compared to other materials commonly used in biorefineries, such as birch wood (26%), peanut shells (25%), or tea waste (17%) (Aliaño-González et al. 2022). In addition, olive wood contains 36.01 α-cellulose and 58.58 holocellulose compared to olive pits at a yield of 33–42% and olive pomace with a yield of 17.37–24.14% (Salem et al. 2007; Dermeche et al. 2013; Garcia-Maraver et al. 2013). Cellulose is a naturally occurring unbranched polymer with repeated glucose $(C_6H_{10}O_5)_n$ units, linked together by β 1 → 4 glycosidic bonds (Seddiqi et al. 2021). Because of different packing and

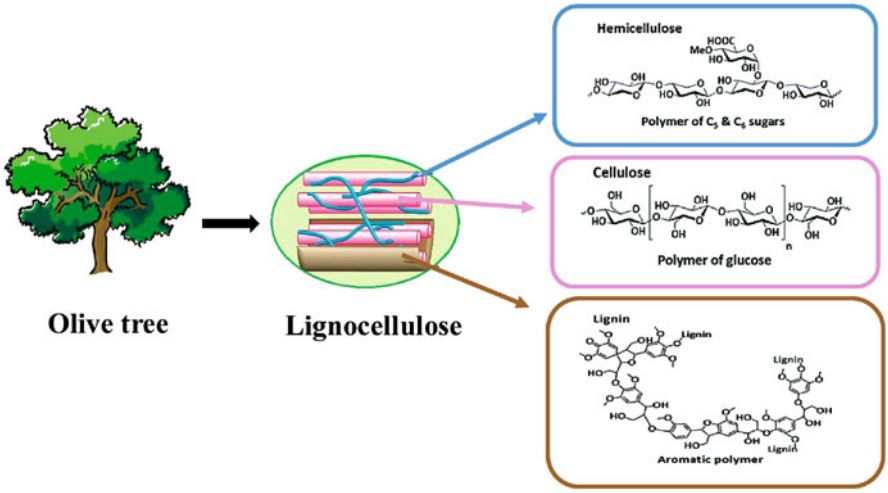


Fig. 13.2 Structure of lignocellulose biomass with the major components

aggregation of cellulose chains, which differ according to cellulose-producing organisms, the structure of cellulose is complicated. Cellulose has three hydroxyl groups in each glucose residue with a degree of polymerization based on glucose units ranging from 1000 to 15,000, according to the source and treatments of the cellulose (e.g., 10,000 in native wood) (Nechyporchuk et al. 2016; Seddiqi et al. 2021).

13.7.1.2 Hemicellulose

Hemicelluloses are macromolecules consisting of the most characteristic parietal components of plants. These macromolecules represent the second most prevalent polysaccharides in nature, wherein xylan is one of the main constituents of this polymer. There are several sources of hemicelluloses, but the most important one is wood. The principal role of hemicellulose is to serve as a link between cellulose and lignin in the cell walls of plants (Cheng and Deming 2011). The content of hemicellulose in olive tree is approximately 15.45%, while olive kernels contain 35–43% and for olive pomace 7.92–11.00% (Salem et al. 2007; Dermeche et al. 2013; Garcia-Maraver et al. 2013). The hemicelluloses are short heteropolysaccharides with about 50–300 units of glycosides (Martel et al. 2010). The functional groups of hemicelluloses contain pentoses, hexoses, hexuronic acids, and acetyl groups, in addition to small amounts of *L*-rhamnose and *L*-fucose. These functional groups can be linked into a series of hemicellulose polysaccharides with diverse structures, linear or highly ramified (for example, xylans, mannans, xyloglucans, β-1,3;1,4-glucans, and galactans). The abundance of these hemicellulose polysaccharides differs significantly between different biomass sources (Ruiz et al. 2017).

13.7.1.3 Lignin

A useful starting point would be a definition of lignin, since they represent a class of polymers of considerable diversity (Ralph et al. 2004). Lignin represents a distinctive aromatic polymer in the cell walls of plants, providing rigidity and mechanical support for the plant, aiding in the transport of water and solutes, as well as playing a role in the protection of the plant from pathogens. Lignin contributes approximately 15–40% of plant biomass (Del Río et al. 2020). For olive bioproducts, we have an amount of 25.30% in olive wood and 15–23% in olive kernels, while olive pomace contains 0.21–14.18% (Salem et al. 2007; Dermeche et al. 2013; Garcia-Maraver et al. 2013). The structure of lignin is diverse, and the specific chemical units vary with the plant source material. Nevertheless, nearly all native lignins have a large fraction of β-aryl ether fragments linked by so-called "β-O-4" bonds, which contain a secondary benzylic and a primary aliphatic alcohol in addition to the characteristic alkyl aryl ether. The three major precursors of the lignin polymer are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Das et al. 2018; Chio et al. 2019).

13.7.2 Application

As a consequence of the overwhelming demand for fossil fuels and their limited availability, new alternatives for energy and chemicals are required as soon as possible. Hence, the exploitation of the natural plant resource, lignocellulose, for the production of bioethanol and energy has become a heated topic in various fields. One of the main processes for the generation of bioethanol is the transformation of cellulose and hemicellulose from lignocellulosic materials. However, a significant amount of lignin may be kept as a by-product after bioethanol production owing to its low reactivity and commercial value. In addition, lignin is also considered a waste in the paper pulp industry. Cellulose represents a renewable, biodegradable, and nontoxic material with a low production cost compared to synthetic biopolymers. Moreover, it constitutes a vast source of ecological and biocompatible products (Nechyporchuk et al. 2016)**.** For tissue engineering, cellulose, as an additive or primary scaffold material, must have mechanical properties consistent with real tissues, enhance porous structures for scaffolds, or provide anchor sites for osteoblasts and fibroblasts (Seddiqi et al. 2021). In the pharmaceutical industry, they have an extensive application history wherein it has been used as a tablet coating whenever it is mixed with various excipients for oral administration. Even with such a long history of use in tablet manufacturing, research is continuously underway on the possible use of cellulose and its derivatives in advanced drug-loaded systems in terms of tablet dissolution rate as suitable excipients or sustained drug release as novel drug carriers (Abeer et al. 2014; Seddiqi et al. 2021).

13.8 Conclusion

This chapter has been encouraged by the raising generation of wastes and by-products derived from the olive production and the olive oil industry in the last years. Nevertheless, we highlight in this chapter that olive by-products are not a waste but a source of useful ingredients exploitable in several fields. In fact, the by-products of *Olea europaea* L. constitute a matrix containing many bioactive molecules such as unsaturated acids, phenolic compounds, phytosterols, tocopherols, and squalene. In fact, these substances are responsible for the many effects on human health. The chemical characteristics, functional or medical food properties, and biological activities of these compounds are presented above in order to highlight how the olive tree can be a food resource of great scientific and health interest.

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Chapter 14
Fruit Pomaces as Valuable By-Products of Wine and Cider Industries

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Abstract This chapter discusses the composition of fruit pomaces, namely, apple and grape pomaces, as well as potential future industrial uses. Additionally, it provides an overview of the extraction techniques used to value bioactive substances. The main composition of these fruit pomaces and the use of the resulting compounds in various industrial sectors, such as the food, cosmetics, pharmaceutical, and feed industries, are additional significant subjects of the chapter. The most effective extraction methods now in use are compared, and the potential functionality of the molecules produced is also discussed.

Keywords Pomace · Green extraction · Extraction yield · Bioactive compounds · Industrial application

14.1 Introduction

It is in recent years that the interest in sustainable development in the food industry has increased with one major problem correlated to the generation of agro-industrial waste. A shift towards a sustainable economic cycle based on more renewable practices and reduced production and consumption of environmental impacts is of paramount importance. As such, an acute problem in the food industry is represented by the recovery of valuable components from food waste.

Pomace is the most important by-product in the production of wine and cider. It is often produced in large quantities and therefore represents an enormous economic and environmental burden for industry and society. Hence, the constant search for novel valorization methods of by-products is essential (Gowman et al. 2019).

According to the Food and Agriculture Organization (FAO), apples ranked third globally (after bananas and watermelons) in terms of production, with 87.24 million tons in 2019 (Faostat 2021). Approximately 35% have been processed into juice and cider, producing a rate of over four million tons of apple pomaces (AP). A processing technique is used depending on the apple type. Furthermore, for every liter of apple juice, around 0.44–0.48 kg of AP is produced (Martau et al. 2021). Statistics show that the world's largest apple producer, China, provides more than one million tons of AP each year. In the European Union, Germany and Poland are among the major producers with postindustrial organic waste of over 0.70 million tons. Additionally, small amounts of AP (ranging between 13 and 20,000 tons per year) are generated by regions such as Brazil, Spain, and New Zealand (Golebiewska et al. 2022).

The major by-product of the winemaking sector is grape pomace (GP). Grape cultivation reached in 2019 a world production of 78.77 million tons, of which 57% were used only in the wine sector. The peels (skins), seeds, and stems that remain after the crushing, draining, and pressing procedures constitute the majority of the pressed grape residue (which encompasses approximately one-fifth of the grape weight). Therefore, almost six million tons of GP has been generated and required

treatment (Oiv 2021). As stated in the 2019 Statistical Report on World Vitiviniculture published by the International Organisation of Vine and Wine, 39% of the world's total grape production was generated in Europe, followed by Asia and America with 34% and 18%, respectively.

Skin and flesh constitute 95% of AP, followed by seeds and stems (2–4%). Depending on the species, region of origin, and previous processing techniques, it contains a wide range of different nutrients. The beneficial proprieties are primarily attributable to the antioxidant activity of polyphenols, such as phenolic acids (especially chlorogenic acid) (Pollini et al. 2022), flavonoids (catechins, epicatechins), dihydrochalcone (phlorizin), and flavonols (quercetin glycosides) (Gorjanović et al. 2020) as well as to the physicochemical and rheological properties (emulsion stability) of the dietary fiber demonstrated in the literature (Schmid et al. 2020b).

Fibers, polyphenolic compounds, colorants, and minerals are considered among the most valuable constituents of GP. Hence, GP represents a significant source of biological compounds, especially polyphenolic compounds, such as phenolic acids, flavonoids, stilbenes, tannins, and proanthocyanidins, which account for the antioxidant potential of grape pomace (Antonic et al. 2020a).

It is the disposal of apple and grape pomaces that produces sustainability hazards including groundwater and surface-water pollution and negative effects on biodegradation during the harvest season, because of low pH and microbial contaminants. Furthermore, there is significant interest in using the predominant bioactive constituents of GP and AP, such as dietary fiber (Juráček et al. 2021) and polyphenols (Caponio et al. 2022) as fortification elements in different types of novel products as agricultural sustainability and consumer expectations become more important. One method of exploiting these valuable by-products is the dietary intake of GP in animal diet, modifying the products' chemical properties by extending shelf-life due to the improvement of oxidative stability (Caponio et al. 2022). Another approach represents the incorporation of GP in dairy and meat products, increasing their antioxidant capacity and total phenolic content (Baroi et al. 2022; Antonic et al. 2020b). Moreover, GP has also been successfully incorporated into other plant-based food products (Goulas et al. 2021).

Taking into consideration the higher level of moisture (over 70%) and biodegradable organic load caused by the chemical and biochemical oxygen requirement of AP and GP, the most common disposal method is to directly discard the by-product to the soil in a landfill, leading to severe environmental pollution problems (Lyu et al. 2020). When considering the storage extension, such a perishable product requires refrigeration. However, the demanded space and energy make this process inefficient and economically unviable (Barreira et al. 2019). Therefore, AP and GP could only be submitted to a drying process (up to 10% moisture content) that would allow a more extended storage period and less demanding conditions, but even so, the financial requirements are high due to the high energy consumption.

For a variety of bioenergy applications, such as the production of intermediate bioenergy carriers (e.g., biogas and pyrolysis oil) (Hernández et al. 2021) and

materials (e.g., biochar and activated carbon) (Golebiewska et al. 2022), raw or processed forms of AP and GP could be taken into consideration.

In addition, AP has the potential to be a source of compounds that result in nontoxic, environmentally friendly biopolymers that have been used to produce packaging, plates, cup materials, biodegradable films, and 3D objects (Lyu et al. 2020).

The valuable AP and GP compounds can be extracted with the aid of various conventional or nonconventional technologies (involving ultrasounds (Kumar et al. 2021), enzymes (Cascaes Teles et al. 2021), supercritical fluid extraction (Ferrentino et al. 2018)), transforming the by-product into industrial commodities such as pectin, fibers hemicellulose, oligosaccharides, and phenolic compounds.

14.2 Pomace Structure

14.2.1 Grape Pomace Structure

GP results following grape pressing in the vinification process and comprises 10–20% of the total grape processed (Gurumeenakshi et al. 2021). This by-product consists of seeds (38–52%), pulp, husks (approximatively 5–10%), stalks, and leaves as the primary elements of GP (Meini et al. 2019).

The composition of this by-product is directly influenced by grape species, planting, growing, and processing steps (crushing and pressing) (Arslan et al. 2018). Despite being highly invasive, the extraction technique does not appreciably alter the chemical composition in terms of bioactive chemicals. GP is mainly characterized by a seedless component (I fraction: especially skin, residual pulp, and stems) and seeds themselves (II fraction). Both fractions comprise a considerable quantity of dietary fiber (concentrations between 43% and 75%, with a preponderance in seeds) (Costa et al. 2019) and oil (10–20%) (Spinei and Oroian 2021).

Nevertheless, the matrices are abundant in bioactive compounds (Bordiga et al. 2017), with the major constituent being represented by phenols (60–70% in seeds and 30–35% in the rest of the compounds) (Bordiga et al. 2017). Pectins and cellulose are the indigestible fractions with a predominance in seeds counting for 80% sugar-free fraction (Cecchi et al. 2019).

14.2.2 Apple Pomace Structure

The composition of AP is extremely reliant on the method of production, apple cultivar, and the harvest season. The pressing of apples is an essential step in cider making and results in approximately 20–25% by-products. Furthermore, AP is a heterogeneous mixture composed of skin and flesh (95%), seeds (2–4%), and stems (1%).

Despite the extraction process, many of the significant substances present in apples are still found in the AP. Compounds include fibers (a range between 45% and 60%, pectin being the most important) and polyphenols (it is estimated that 82–99% of polyphenols remain in the AP with an essential antioxidant and antibacterial activity) (Li et al. 2020).

Apple seeds possess a high oil content (ranging from 12% to 27.5%, with unsaturated fatty acids and tocopherols as dominant) (Antonic et al. 2020a) and proteins (30–35%) (Sudha 2011; Lobo and Dorta 2019). A considerable amount of phosphorus, potassium, magnesium, calcium, and iron have also been found in apple seeds (Vidović et al. 2020).

However, due to its techno-functional proprieties, such as low water solubility and adsorption, alongside low thickening and gelling proprieties, the industrial application in food products is limited (Zlatanovic et al. 2019; Schmid et al. 2020a). By making changes to the cell wall's structure through chemical (Lang et al. 2022), enzymatic (Gama et al. 2015), thermal (Zlatanović et al. 2019), and mechanical treatments, these restrictions can be lifted.

14.3 Chemical and Nutritional Composition

14.3.1 Carbohydrates

As mentioned, on an overall, fruit pomace, a by-product of the wine and cider industry, is a rich source of carbohydrates, nutrients, and bioactive components. Healthwise, carbohydrates from plants are the preferred energy source for the human body. They include sugars (monosaccharides and disaccharides), oligosaccharides, starches, non-polysaccharides (mainly cellulose, hemicellulose, and pectin), and fibers (Blanco and Blanco 2017).

Apple pomace is rich in carbohydrates 48.0–83.8%. There are simple sugars such as glucose (22.7%), fructose (23.6%), galactose (6% to 15%), sucrose (1.8%), arabinose (14–23%), and xylose (1.1%) present in that substance (Dhillon et al. 2013).

Additionally, fermentable sugars, such as fructose (19.2%) and sucrose (1.0%) (Magyar et al. 2016) present in apple pomace, are considered a cost-efficient carbohydrate source for lactic acid bacteria and yeasts (Martau et al. 2021) used in different fermented products. Similarly, Fernandes et al. characterized apple pomace as a functional and healthy ingredient in food products with carbohydrates as the major component (720 g/kg dry weight basis). These carbohydrates contain 180 g/kg of free sugars, mainly fructose, and 530 g/kg of polysaccharides with glucose, arabinose, xylose, and galactose as the most abundant sugars (Fernandes et al. 2019b).

Apple pomace includes about 14% starch along with nondigestible glycosidic polymers. Apparently, 40–48% of amylose makes up the majority of apple starch (Szalay et al. 2013).

It is well recognized that the type of waste, grape variety, cultivation environment, and winemaking technique all have a significant impact on the composition of grape pomace (Garrido et al. 2011). Grape pomace has a high water content right after production, which affects its physical and chemical properties and encourages microbial contamination. As a result, drying grape pomace and delaying those processes are crucial (Garcia-Lomillo and Gonzalez-Sanjose 2017).

There are differences to be noted, as white and rose wines are produced through must fermentation, whereas red wine production involves the fermentation of the grape must, pulp, skins, and seeds. This indicates a wide range in the composition of grape pomace and poses a considerable challenge to its value (Jin et al. 2019). In this respect, Rondeau et al. reported on the composition of grape pomace from red and white winemaking of the common grape (*Vitis vinifera*) from eight different French vineyards (Rondeau et al. 2013). Large variations were seen depending on the cultivar and grape varieties, ranging between 20% and 46% sugar content, with the majority of that being glucans and xyloglucans and only a trace amount of pectinaceous polysaccharides.

In the Pacific Northwest region of the USA, Deng et al. analyzed grape pomace chemical composition in five white and red *Vitis vinifera* varieties from different wineries. In this study, the two white wine grape pomace varieties had significantly higher soluble sugar contents, about 56% for Muller-Thurgau and 78% for Morio-Muscat, than those of red wine grape pomace, with ranges of only 1.3–1.7%. The unfermented juice residue attached to white wine grape pomace rendered a considerably higher amount of soluble sugar than those in red wine grape pomace (Deng et al. 2011).

Jin et al. analyzed eight commercial white and red pomace samples from various wineries in Virginia, USA, in order to assess the potential uses of grape pomace. The results showed a significant glucose variation, between 2.09 and 53.3 g/kg grape pomace and fructose between 3.79 and 52.9 g/kg grape pomace. The variety and winemaking technology determined this considerable variation in monosaccharides. Higher glucose (26.34 g/100 g) and fructose (8.91 g/100 g) contents are found in white grape pomace, making it a potential candidate ingredient in fortified products. Because yeasts mostly utilize these sugars during the fermentation phase of the red wine manufacturing process, the amount of soluble sugars, glucose, and fructose in red grape pomaces is typically minimal (Jin et al. 2019).

In a study by Beres and colleagues regarding antioxidant dietary fiber recovery from Brazilian Pinot noir grape pomace, the authors reported a carbohydrate content of 19.68 g/100 g, of which 3–10% are polysaccharides. The total sugar content in the grape pomace extract varied between 2.26% and10.9%, depending on the temperature of polysaccharide extraction (Beres et al. 2016).

Other examples include the flour from grape pomace grinding used in baking or cooking. A study from Brazil, Sousa et al. state that, in grape pomace flour, the carbohydrates accounted for 29.20 g/100 g sample, and fructose was present in the most significant amount (8.91 g/100 g), followed by glucose (7.95 g/100 g). There were no significant values for sucrose in flour obtained from grape (*Vitis vinifera* L.) of the Benitaka variety (Sousa et al. 2014).

As such, carbohydrates are found in apple and grape pomace in large amounts, with a significant difference due to the morphological structure of those fruits.

14.3.2 Proteins

All living organisms contain proteins, which are extremely complex materials. In addition to being directly involved in the chemical processes necessary for life, proteins have significant nutritional importance.

Numerous researches have examined the chemical content of apple pomace, and they have found that the amount of protein varies depending on the type of processing and apple variety used to make cider. For instance, Wang et al. (2019) discovered that apple pomace mixture was suitable for use in yogurt because it included 3.8% protein (Wang et al. 2019b). Other authors state that protein content in apple pomace powder is around 1.2% (Jannati et al. 2018) and 2.4% (Ktenioudaki et al. 2013). In terms of usage, apple pomace, with a 4.50% protein content, was used by Younis and Ahmad as an ingredient of buffalo meat sausages (Younis et al. 2015). In contrast, the protein content of apple pomace extract as a sustainable food additive was 50 g/kg of its dry weight (Fernandes et al. 2019b).

Only tyrosine is present in modest amounts in apple seed proteins, which are balanced and high in sulfur amino acids. Comparing to the whole egg protein, the lysine content of apple seed proteins can render it suitable as complementary cereal proteins (Yu et al. 2007).

However, unlike legumes and nuts, grape pomace is not regarded as a necessary source of protein, despite the fact that grape seeds contain 11–13% protein (Shinagawa et al. 2015). Depending on the grape variety, region, and fertilization procedures, the total amount of protein and the amino acid composition of grape seed protein might differ greatly (Yu and Ahmedna 2013). High quantities of essential amino acids were identified in grape seed protein, with glycine, glutamic acid, and aspartic acid being the most prevalent amino acids (Alvarez-Ossorio et al. 2022). Grape seeds comprise 40% fibers, 10–20% lipids, and 10% proteins, and the rest are sugars, polyphenolic compounds, and minerals (Beres et al. 2017).

Bravo and Saura-Calixto analyzed the composition of grape pomace, obtaining 12–14% protein content and less than 3% soluble carbohydrates (Bravo and Saura-Calixto 1998), while Spinei and Oroian found grape pomace as a dietary source of pectin (Spinei and Oroian 2021).

Also, Shinagawa et al. observed that the grape seed consists of 11% protein, 35% fiber, 3% minerals, and 7% water (Shinagawa et al. 2015), while other authors found that grape seeds contained 40% fibers, 10–20% lipids, and 10% proteins, and the rest are sugars, polyphenolic compounds, and minerals (Beres et al. 2017).

Moreover, Hanh et al. observed that the decrease in total fiber content may have contributed to the little rise in protein and fat content in grape pomace after the enzymatic treatment. According to the authors of this study, wheat flour (11%) has higher protein and fat content than grape pomace (8–8.2% dry basis), which is

utilized in baking (Hạnh et al. 2021). Similar to cereals, wine pomace has an amino acid composition that is high in glutamic and aspartic acids and low in tryptophan and sulfur-containing amino acids (Baca-Bocanegra et al. 2021).

In terms of the protein content for the red wine grape pomace, Airén and Tempranillo, Mora-Garrido et al. found that it varied between 7% and 10% and that there were no significant variations in the protein content between the two periods before and after washing, according to diffusion bands, indicating that the protein content was not reduced by the washing (Mora-Garrido et al. 2022).

Generally speaking, depending on the grape variety and harvesting conditions, the protein level in wine pomace may range from 6% to 15% (dry matter) (Bordiga et al. 2019). Skins from wine pomace are somewhat more protein-dense than seeds extracted from wine pomace, yet both are very high in protein (Gazzola et al. 2014; Garcia-Lomillo and Gonzalez-Sanjose 2017). Alanine and lysine are abundant in skin proteins, while they are absent from seed proteins (Igartuburu et al. 1991).

However, apple pomace is a poor source of this important nutrient compared with grape pomace due to the morphological and chemical compositional differences between apples and grapes.

14.3.3 Fatty Acids

By-products of grape and apple processing are abundant in bioactive phytochemicals in the form of unsaturated fatty acids, with the potential to be used as functional dietary additives (Yu and Ahmedna 2013). For both wine and cider pomace, seeds have the major fatty acid contribution.

For instance, seeds from wine pomace have fatty acid contents ranging between 14% and 17% (Gul et al. 2013; Mironeasa et al. 2016). The predominant fatty acids in grape seed oil are linoleic acid, oleic acid, and palmitic acid (Fernandes et al. 2013; Zhao et al. 2019; Mohamed Ahmed et al. 2020). However, since large levels of linolenic acid can result in an unpleasant odor and flavor, lesser levels are ultimately preferable in edible oils (Ozcan and Al Juhaimi 2017).

Kolláthová et al. analyzed grape pomace of Green Veltliner, Pinot Blanc, and Zweigelt from Slovakia and Austria and characterized their specific fatty acid profiles. Some similarities in the fatty acid composition of grape pomace were found, despite the large variances between the countries and between the cultivars within each country. Oleic acid was the most prevalent in the grape pomace from Slovakia and Austria. The samples also contained polyunsaturated fatty acids, which were represented by linoleic acid and monounsaturated fatty acids (Kolláthová 2020).

Other studies by Ribeiro et al. (2015) reported an average polyunsaturated fatty acid concentration in grape pomaces around 72.86%, with the predominance of linoleic (60.04%) and α-linolenic (13.64%) acid, followed by oleic (12.97%) and palmitic (6.72%) acids. Stearic acid was present in the analyzed pomaces below 5% (Ribeiro et al. 2015). Russo et al. studied the fatty acid profile of six grape pomaces with similar results reporting that grape stalk contained 21% palmitic, 4.6% stearic,

10.7% oleic, 35.4% linoleic, 13.4% α-linoleic, and 11.3% behenic acid (Russo et al. 2017).

It was also recorded that in grape stalk, saturated fatty acids, such as palmitic and stearic acid, are predominant. The high palmitic acid content in pomaces may be due to surplus saturated compounds in their waxy structure (Gülcü et al. 2019). The agroclimatic conditions of the growing regions have an impact on the fatty acid content in grape by-products (Garcia-Lomillo and Gonzalez-Sanjose 2017).

Apple pomace contains about 4–7% seeds, which have a higher lipid content than grape pomace. In apple seeds, oil yield ranges from 12% to 27.5% (Górnaś et al. 2014). Around 90% of the fatty acids in apple seeds are unsaturated, with oleic and linoleic acids making up the majority. Apple seed oil contains 10% saturated fatty acids, with palmitic acid serving as the primary one. Tocopherols and phytosterols are also crucial components of apple seed oils (Górnaś and Rudzińska 2016). Additionally, the cyanogenic glycoside amygdalin found in apple seeds may be harmful at certain quantities (Fidelis et al. 2019).

The linoleic acid was the main component in Limón Montés (60.78%), followed by Riega (60.01%). Solarina seed oil was the one with the highest content in total sterols (558 mg/100 g of oil), while Blanquina presented the lowest amount (166 mg/100 g of oil) (Bada et al. 2014). In several industrial fields, the active substances isolated from apple pomace, such as the derivatives of benzoic and cinnamic acids, can be employed as nontoxic, easily accessible, and biodegradable anticorrosion agents or wood protectors (Golebiewska et al. 2022).

Overall, the lipid fraction in apple and grape pomace has an intriguing fatty acid composition that is high in polyunsaturated and monounsaturated fatty acids and low in saturated fatty acids.

14.3.4 Phenolic Compounds

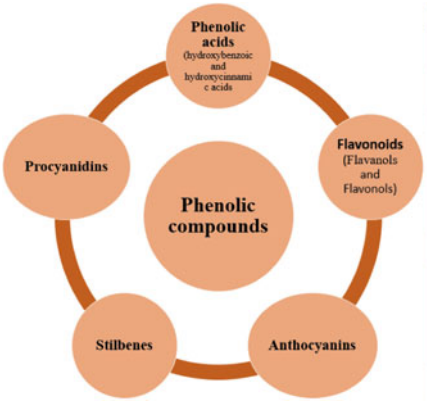
Due to increasing consumer attention paid to sustainable agriculture and to the use of natural compounds to the detriment of synthetic ones, there is an intense concern for the use of fruit by-products for the development of innovative value-added products, such as food additives, nutraceuticals, functional food ingredients, food supplements, cosmetics, fertilizers, and biomass for biofuels (Kalli et al. 2018). Valorization of by-products resulting from fruit processing through the extraction of biologically active molecules, which will be used for innovative product applications in the food, cosmetic, or pharmaceutic industry, has been an intensively studied field in the last decades (Alexandri et al. 2021; Fierascu et al. 2020).

Polyphenolic compounds from the peel, pulp, or seeds of the fruit represent the most important bioactive compounds in the fruit pomace. During processing, polyphenols are partially transferred to the resulting juices, but considerable amounts remain in the peel, and therefore, most polyphenols are also found in the pomace (Waldbauer et al. 2017). As mentioned, the composition of fruit pomace depends on the type of fruit, species, and cultivar and climatic and agronomic factors as well as

processing and storage operations (Antonic et al. 2020a; Guiné et al. 2021). Immediately after production, the chemical stability of the fruit pomace is affected by the high water content that favors microbial degradation (Garcia-Lomillo and Gonzalez-Sanjose 2017). Therefore, the immediate drying of the fruit pomace after pressing represents a possibility of preserving the polyphenols because the degrading enzymes (polyphenol oxidases and peroxidases) which causes the brown discoloration of pomace after pressing are inactivated (Waldbauer et al. 2017). To this end, gentle drying methods like the freeze-dried method are preferred because it avoids the formation of 5-hydroxymethylfurfural by the thermal degradation of sugars during the oven drying process (Garcia-Lomillo and Gonzalez-Sanjose 2017).

Numerous studies have been carried out on the identification of polyphenols in the fruit pomace (Arraibi et al. 2021; Gumul et al. 2021; Li et al. 2020; Milinčić et al. 2021; Peixoto et al. 2018). As a consequence, the main classes of phenolic compounds identified in fruit pomace are phenolic acids (hydroxybenzoic and hydroxycinnamic acids), flavonoids (flavanols, flavonols and dihydrochalcones), anthocyanins, stilbenes, and procyanidins (Fig. 14.1). The representative phenolic compounds from each class are specific for each type of pomace.

Apple pomace (AP) contains large amounts of polyphenols (31–51%) (Lyu et al. 2020). Thus, the polyphenolic profile of fresh apple pomace is similar to fresh apples, showing high contents of phenolic acids such as chlorogenic, protocatechuic, salicylic, caffeic, and p-coumaroylquinic acids, flavanols ((+)-catechin, (−)-epicatechin, procyanidins B1, B2, B3, B5, and C1), flavonols (rutin, quercetin, isorhamnetin, kaempferol, rhamnetin and their glucoside, galactoside, arabinoside, xyloside, rutinoside, and rhamnoside derivatives), dihydrochalcones (phloretin and phloretin glucoside derivatives), and anthocyanins (cyanidin-3-O-galactoside, cyanidin-3-O-hexoside) (Fernandes et al. 2019b; Gumul et al. 2021; Lyu et al. 2020; Perussello et al. 2017; Waldbauer et al. 2017). Phloridzin represent the most predominant polyphenol in dry apple pomace (Kammerer et al. 2014) and a good marker for the identification of dry apple pomace (Waldbauer et al. 2017).



Phenolic compounds
Hydroxybenzoic acids: gallic acid, p-hydroxybenzoic acid, protocatechuic acid, syringic acid
Hydroxycinnamic acids: caffeic acid, p-coumaric acid, ferulic acid, synaptic acid, caftaric acid, coutaric acid, fertaric acid
Flavanols: catechin, epicatechin, epicatechin gallate
Flavonols: kaempferol, quercetin, isorhamnetin-3-O-glucoside, kaempferol-3-O-glucoside, quercetin-3-O-glucoside, quercetin-3-O-galactoside, quercetin-3-O-glucuronide, quercetin-3-O-rhamnoside, rutin
Dihydrochalcons: phloretin, phloretin-2-O-glucoside, phloretin-2-O-xylosyl-glucoside, phloretin-pentosylhexoside, phloretin-hexosyl-hexoside, 3-hydroxyphloretin-2′-O-xylosyl-glucoside, 3-hydroxyphloretin-2′-O-glucoside
Stilbenes: trans-resveratrol
Anthocyanins: cyanidin, cyanidin-3-O-glucoside, cyanidin-3-O-p-coumaroylglucoside, delphinidin, delphinidin-3-O-glucoside, delphinidin-3-O-acetylglucoside, malvidin, malvidin-3-O-glucoside, malvidin-3-O-acetylglucoside, malvidin-3-O-p-coumaroylglucoside, peonidin, peonidin-3-O-glucoside, peonidin-3-O-acetylglucoside, peonidin-3-O-p-coumaroylglucoside, petunidin, petunidin-3-O-glucoside, petunidin-3-O-acetylglucoside, petunidin-3-O-p-coumaroylglucoside
Procyanidins: procyanidin B1, procyanidin B2, procyanidin B3, procyanidin B5, procyanidin C1

Fig. 14.1 The main classes of phenolic compounds identified in fruit pomace

AP residues result from the industrial production of apple juices, purees, syrup, and cider, with AP resulting from the production of clear juice showing high amounts of polyphenols due to the use of pectinases during the clear juice production process which favor the release of polyphenols from the apples (Waldbauer et al. 2017).

During winemaking of red grapes, a gentle but prolonged hydro-ethanol extraction of polyphenols from grapes occurs resulting in red wines and the residue left after fermentation, namely, grape pomace (GP). GP consists of skins and seeds and still contains high amounts of polyphenols (Fontana et al. 2013). GP resulting from the winemaking of rose and white wines shows a high variation of polyphenolic composition, because the solid residue resulted after pressing is removed before the juice fermentation (Antonic et al. 2020a).

The most abundant polyphenolic compounds identified mainly in red GP are anthocyanins (cyanidin, cyanidin-3-O-glucoside, cyanidin-3-O-*p*-coumaroylglucoside, delphinidin, delphinidin-3-O-glucoside, delphinidin-3-O-acetylglucoside, malvidin, malvidin-3-O-glucoside, malvidin-3-O-acetylglucoside, malvidin-3-O-*p*-coumaroylglucoside, peonidin, peonidin-3-O-glucoside, peonidin-3-O-acetylglucoside, peonidin-3-O-*p*-coumaroylglucoside, petunidin, petunidin-3-O-glucoside, petunidin-3-O-acetylglucoside, petunidin-3-O-*p*-coumaroylglucoside) hydroxybenzoic acids (gallic, *p*-hydroxybenzoic, protocatechuic, syringic acids) and hydroxycinnamic acids (caffeic, p-coumaric, ferulic, synaptic, caftaric, coutaric, fertaric), flavan-3-ols (catechin, epicatechin, epicatechin gallate), flavonols (kaempferol, quercetin, isorhamnetin-3-O-glucoside, kaempferol-3-O-glucoside, quercetin-3-O-glucoside, quercetin-3-O-galactoside, quercetin-3-O-glucuronide, quercetin-3-O-rhamnoside, rutin), stilbenes (trans-resveratrol), procyanidins (procyanidin B1 and B2), and condensed tannins (up to 52% dry weight) (Fontana et al. 2013; Hogervorst et al. 2017; Milinčić et al. 2021; Peixoto et al. 2018; Spinei and Oroian 2021).

To extract polyphenolic compounds from fruit wastes, green extraction techniques such as sub−/supercritical, ultrasound-, microwave-, and enzyme-assisted extraction methods are utilized. These techniques adhere to green chemistry principles (Kalli et al. 2018; Monari et al. 2020). Valuable extracted polyphenols can be directly formulated as nutraceuticals due to their therapeutic properties, including antioxidant, anti-inflammatory, antimicrobial, and anticancer potential or even antidepressant activity (Antonic et al. 2020a; Fierascu et al. 2020) or can be used as functional ingredients for the food industry (cookies, ciders, and meat products) (Fernandes et al. 2019b).

14.3.5 Dietary Fibers

In addition to phenolic compounds, fruit pomace contains components that cannot be digested by the human enzymatic system named dietary fibers (Waldbauer et al. 2017). These are a category of carbohydrates, 70% of them being classified into

insoluble fibers, such as cellulose, hemicelluloses, and lignin, and 30% represent soluble fibers (pectin, inulin, gums, and mucilage) (Perussello et al. 2017).

In this respect, grape pomace (GP) is a rich source of fiber, such as cellulose, hemicellulose, lignin, and pectin. Red grape pomace is richer in fiber than white grape pomace, while grape seeds contain higher amounts of fibers compared with grape skin (Antonic et al. 2020b). As such, the pomace fiber extract play an important role in various foods and pharmaceutical products (Lyu et al. 2020) than the pomace.

Pectin is a soluble fiber used as a common additive in the food industry, acting as a gelling, emulsifying, and thickening agent in numerous food products such as confectionery, bakery jellies, yogurts, and beverages (Perussello et al. 2017). Apple pomace is one of the main fruit sources of pectin, its extraction being considered a reasonable approach to AP use (Masuelli and Blumenberg 2020). Common sources for extracting fibers (mainly pectin) are apple pomace and citrus peel, but grape pomace represents an alternative to conventional ones (Spinei and Oroian 2021). Pectin has beneficial effects on human health reducing the cholesterol and absorption of glucose (Blanco-Perez et al. 2021). Also, pectin in grape pomace binds chemically to polyphenolic compounds forming antioxidant dietary fibers, thus increasing the pomace antioxidant potential (Antonic et al. 2020a; Perussello et al. 2017).

The common pectin extraction methods from pomace include enzymatic, mechanical ultrasonic homogenizing, and chemical extractions. Usually, pectin is obtained from pomace by acid extraction and precipitation using alcohols. The use of special extraction and purification conditions leads to obtaining pectin with special physical properties for food industry (e.g., swelling capacity used to modify the textural properties of the food product or oil retention capacity for the replacement of fat in bakery products) (Lyu et al. 2020; Spinei and Oroian 2021). Grape pomace fibers can be used as filler in polymer composites, replacing the synthetic fibers in composites for specific applications, thus contributing to lowering the cost of the final material (Monari et al. 2020).

14.3.6 Organic Acids

Organic acids have been used as preservatives in food processing, pharmaceutical, and cosmetic industries (Panda et al. 2019). Due to their importance and the necessity to develop a sustainable production sector, different alternative sources to produce organic acids were investigated. In this context, fruit pomace represents an ideal low-cost substrate for sustainable production of organic acids from natural resources which can help to improve the overall economic cost. Organic acids in pomace are both free and bound mainly with potassium and calcium (Egorov et al. 2021).

The transformation of apple pomace for the bio-production of organic acids is achieved through sequential hydrolysis and fermentation using different microorganisms (Munekata et al. 2021). Thus, fruit pomace shows several attributes as a raw

material for organic acid production, such as (1) high content of glucose, fructose, and polysaccharides such as cellulose and hemicelluloses which can be enzymatically hydrolyzed to fermentable monosaccharides, (2) presence of metal ions (Mg, Mn, Fe, etc.) which could limit the cost of nutrient supplementation for fermentation media, and (3) high moisture content (Dhillon et al. 2013).

Therefore, some studies have been carried out to investigate the use of AP in the production of organic acids, such as acetic acid (Parmar and Rupasinghe 2013; Vashisht et al. 2019), propionic acid (Piwowarek et al. 2021), citric acid (Ali et al. 2016), and fumaric acid (Das et al. 2015), or the use of grape pomace as a recovered source of tartaric acid (Garcia-Lomillo and Gonzalez-Sanjose 2017) and citric acid (Papadakis et al. 2018).

14.3.7 Amino Acids

The amino acid profile of grape pomace is similar to those of cereals, showing high amounts of aspartic and glutamic acids and low amounts of tryptophan and sulfur-containing amino acids (Bordiga et al. 2019), which makes grape pomace optimal for animal feed (Ianni and Martino 2020). The amino acid profile of grape pomace includes aspartic and glutamic acids, alanine, arginine, glycine, leucine, isoleucine, lysine, serine, valine, phenylalanine, proline, tyrosine, histidine, cysteine, and methionine (Nakao et al. 1983). The identified essential amino acids in apple pomace are threonine, valine, leucine, isoleucine, methionine, phenylalanine, and lysine, while alanine, glycine, serine, γ-aminobutyric acid, proline, asparagine, and glutamic acid are considered nonessential amino acids (Farcas et al. 2022). Amino acids are easily oxidized or denatured at high temperatures, and consequently, freeze-dried treatments of pomace ensure high amounts of amino acids (Emami et al. 2018).

14.3.8 Vitamins

Vitamins are essential for plant and animal metabolism, and their deficiency leads to various disorders and diseases. Plants, including fruits and vegetables, are an excellent source of the vitamins, and consequently, these vitamins can also be found in fruit and vegetable products and by-products. Due to the significant loss of vitamins during winemaking, the resulting wine and pomace have a low level of vitamins, thus being unsuitable as a valuable source of vitamins for the human body (Velić et al. 2018). Usually, vitamins (biotin [vitamin H] and nicotinic acid [niacin, vitamin B3]) are enough to support microbial growth during winemaking and low amounts can also be detected in the resulting pomace (Mckay et al. 2010). Some water-soluble vitamins were identified in pomace, such as ascorbic acid, thiamine (B1), riboflavin (B2), nicotinic acid (B3), pantothenic acid (B5), and biotin (B7), depending on the pomace grape variety (Egorov et al. 2021).

14.3.9 Minerals

Minerals are inorganic compounds required in small amounts for various metabolic processes important for the functioning of the human body. Fruit mineral content depends on genetic and environmental factors, cultivation procedures, and soils used for fruit growing (Francini et al. 2022), and consequently, the resulting pomace shows different mineral content. Also, the processing equipment (stainless steel, aluminum, glass, and wood) and applied technological procedures can be sources of wine contamination with Al, Cd, Cr, Cu, Fe, and Zn (Dumitriu et al. 2019).

Apple pomace contains minerals such as P (0.07–0.076%), Ca (0.06–0.1%), Mg (0.02–0.36%), and Fe (31.8–38.3 mg/kg, dry weight) (Lyu et al. 2020), while grape pomace can be considered a good source of Fe (180 mg/kg), Zn (9.8 mg.kg), and K (14 mg/kg) dw (Sousa et al. 2014). Potassium salts, mainly potassium bitartrate, represent a significant amount of the wine pomace (4–14%, dw) (Bordiga et al. 2019). The total amount of minerals in fruits and pomace represents the ash content, which is considered as inorganic residue remaining after removal of water and organic matter (Velić et al. 2018).

14.4 Extraction Methods of Pomace Bioactive Compounds

Starting with the procedure applied for the extraction of valuable wine and apple pomace compounds, it can be decided whether a further application of the resulting extract might be used as a derived food, pharmaceutical, or cosmetic product or as feed, respectively. Table 14.1 summarizes the extraction methods applied to valorize specific compounds of interest in different industrial fields. The different extraction procedures reported so far for the extraction of apple and grape pomaces can be described as follows.

14.4.1 Ultrasound

Conventional extraction methods using organic solvents are still by far a widespread technique with the purpose of extracting bioactive substances (Barba et al. 2016). In addition to the procedures' limitations, which are demonstrated by the oxidation and thermolysis-induced degradation of anthocyanins and other phenolic compounds, the environmental impact and energy costs reduce the efficiency of traditional methods (Bruno Romanini et al. 2021). Therefore, it is advisable to use unconventional technologies such as ultrasound extraction (USN).

In recent times, USN has become more widespread as a stand-alone procedure or as part of the stepwise procedure due to the disruption of plant cell walls by the cavitation effect, which increases heat and mass transfer (Kumar et al. 2021). It is

Table 14.1 Valorizing of grape and apple pomace constituents in other industries

Compound of interest/ source Apple/ grape	By-product used (variety)	Extraction method applied	Extraction yield/concentration of extracted compounds	Advantages	Disadvantages	Type of product where further used	Concentration of interest compound being used	References
Polyphenols/ total phenolic content (TPC)	Grape pomace (merlot and Zelen) flour (GPF)	Dried and milled	n/a	↑Antioxidant properties, ↑stability	Sand feeling in mouth, increased intensity of aftertaste	Bread	GPF = 6–15%	Sporin et al. (2018)
	Grape pomace (Barbera, chardonnay) powder (GPP)	Aqueous extraction	32–58% increase in TPC	↑Antioxidant properties	↓TPC extraction values for Barbera GP than 80% acidified methanol extraction	Cheese (Toma-like, Cheddar)	GPP = 0.8–1.6%	Apostolidis et al. (2007) and Marchiani et al. (2016)
	Grape pomace (Sangiovese) skins	UAE Ethanol/water (4:1 v/v) infusion	TPC_{UAE} = 207.55–259.26 mg GAE/g extract $TPC_{infusion}$ = 130.65–171.48 mg GAE/g extract	↑Antioxidant properties ↑TPC extraction values with UAE (which was further used for kefir fortification)	↓TPC extraction values reported for infusion (not further used for kefir fortification)	Kefir	1–10 mg UAE extract with 10 mL kefir	Carullo et al. (2020)
	Grape pomace (GP) before (GP_{BD}) and after distillation (GP_{AD})	Acidic EtOH/H2O 7:3 v/v double extraction (Bali et al. method)	32–47% recovered phenols	↑Antioxidant properties when GP_{BD} is used ↑Fiber amount	GP_{AD} not suitable for added nutraceutical value (lost of free anthocyanins and ↓total phenols)	Tagliatelle	GP_{BD}(w/w) =7%	Balli et al. (2021)
	Grape seed and grape pomace	Soxhlet extraction followed by ethanolic aqueous extraction/Soxhlet extraction	73%—Oil extraction yield and 153 mg GAE/kg oil 17.4–18.4%—Phenolic compound yield	Higher yields with 2 weeks previous storage of seeds	Low seed oil polyphenol content compared to seed polyphenol content	Cosmetics, as antioxidants	0.1%	Rombaut et al. (2015) and Ferreira and Santos (2022)
	Grape pomace (Barbera)	Microencapsulation (hydrogel)	68% (m/m) total phenolic encapsulation efficiency	pH-controlled release of phenolic compounds Prevention of AGE-related diseases	Alginate interaction with phenolic compounds which led to a lower yield	Microcapsules with 68% polyphenols for preventing AGE-related diseases	25 mL grape extract at 475 mL solution containing 1.5% alginate	Lavelli and Sri Harsha (2019)

(continued)

Table 14.1 (continued)

Compound of interest/ source Apple/ grape	By-product used (variety)	Extraction method applied	Extraction yield/concentration of extracted compounds	Advantages	Disadvantages	Type of product where further used	Concentration of interest compound being used	References
	Grape pomace (GP)	Solid-liquid extraction (1:7 w/v) in acetone 80% and methanol (100%)	810.60 ± 26.40 (mg GAE/100 g raw material	↑Antioxidant activity in the piglet organs	n/a	Piglet feed (TPC content determined after mixture of feed +GP was made; pigs were not fed with the extract)	5% powdered GP	Chedea et al. (2019)
	Red grape pomace (petit Verdot)—RGP	Pressurized liquid extraction (PLE) and enhanced solvent extraction (ESE)	8.2–8.6% (m/m)	PLE—↑ bioactive extract	ESE—a higher temperature (70 °C) limited the recovery of the polyphenol	Bioactive (preservative properties) jute fibers for food packaging	9.6–90% RGP extract (28.8–270 mg)	Cejudo-Bastante et al. (2021)
	Apple pomace (Royal Gala)	Hot water extraction with diluted acetic acid for preventing oxidation	TPC = 3.26 g GAE/kg of apple pomace	Cheap, nontoxic, environmentally friendly, easy implementable on an industrial scale Higher yield than room temperature water extraction	Lower yield than methanol or acetone extractions	Yogurt	3.3%	Fernandes et al. (2019a)
	Grape pomace powder (Muscat Hamburg)—GPP	Methanol (80%) extraction 1: 15 (m/v)	Phenolic acids: 6.6–18.2 mg/kg DM Flavonoids: 33–56.3 mg/kg DM Anthocyanins: 10–26.4 mg/kg DM	Good sensory qualities (best at 4% GPP content) ↑Antioxidant properties, fibers, ash, lipid, proteins	Diminished volume, increased hardness and chewiness at 10% GPP addition	Cake	4–10% GPP	Nakov et al. (2020)
	Grape pomace flour (Niagara Rosada, Maximo, Bordo, Violeta)—GPF	Drying and milling	TPC = 23.2–49.3 mg/kg	Whole pomace used, without oil removal, leading to ↑TPC	Niagara Rosada presented ↓Bioactive compounds	Salmon burgers	GPF = 1–2%	Monteiro et al. (2021), Cilli et al. (2020)

	Dried grape pomace (cabernet sauvignon)	UAE	$TPC_{CS\text{-}DGP}$ = 3415–13,754 mg GAE/kg	Potential use in chocolate spread substitute replacing sugar and milk-derived powder with increased phenolic content	↓Spreadability ↑Firmness Dried grape pomace >10 g/100 g was not sensory accepted	Chocolate spread	DGP = 0.23–15 g/100 g	Acan et al. (2021)
	Grape pomace fresh and fermented (Feteasca Neagra variety)	70% ethanol extraction by modified Squibb repercolation method (1/1 g/mL)	TPI = 114.71–161.58 mg CAE/g dw	↑The maceration process may be responsible for the increased TPI found in fermented grape pomace as opposed to fresh grape pomace	TAnthC ↓ in the fermented grape pomace due to formation of polymeric pigments.	Extracts to evaluate cardioprotective properties by decreasing oxidative stress against ISO-induced myocardial ischemia	1 mL/day p.o. for 7 days	Balea et al. (2018)
Anthocyanins	Grape pomace (Barbera) maltodextrin–encapsulated (GSM)	Drying followed by 60% aqueous ethanolic extraction and encapsulation in maltodextrin	TA = 1136 ± 50 (mg/kg DW) in fortified apple puree	Stability under heat treatment and storage conditions Natural coloring agent and ↑anthocyanin and flavonoid levels	Lower anthocyanin content and stability than black carrot extract	Fortified apple purees	1.4%GSM	Lavelli et al. (2016)
Fibers	Grape pomace (Syrah) powder (GPP)	Drying of the pomace (55–75 °C) and milling (grain size 0.1–0.2 mm)	Crude fibers = 17.55–23.11 g/100 g dwb	↑Crude fiber, proteins, lipid content (highest in 25% GPP muffins)	Gritty texture for muffins with 25% GPP addition	Gluten-free muffins	GPP = 15–25% (75 °C dried GP was used)	Baldán et al. (2021)
	Wine grape pomace (cabernet sauvignon)	Drying and powdering	Fibers—47.7 g/100 g WGPF Polyphenols—41.11 mg GE/g Anthocyanins—1.49 mg C3G/g	Improves glycemia and blood pressure; ↓postprandial insulin levels, ↓oxidative protein damage ↑Handling of oxidative stress	Not influencing serum cholesterol	Wine grape pomace flour (WGPF)—As supplement 20 g/day	20 g/day	Urquiaga et al. (2015)

(continued)

Table 14.1 (continued)

Compound of interest/ source Apple/ grape	By-product used (variety)	Extraction method applied	Extraction yield/concentration of extracted compounds	Advantages	Disadvantages	Type of product where further used	Concentration of interest compound being used	References
	Apple pomace (AP) Grape pomace (GP)	Fiber assay kit	$TDF_{AP} = 53.1 \pm 0.7$ g/100 g $TDF_{GP=}$ 45.9 ± 0.6 g/100 g	High-fiber extrudates	↑TDF = ↓expansion of extrudates	Corn starch extrudates	AP/GP = 50–300-g/kg	Wang et al. (2019a)
	Grape pomace powder	Ethanolic extraction	$TDF_{Riesling} = 52.21$ g/100 g $TDF_{Tannat} = 67.95$ g/100 g	↑Dietary fiber contents	↑Hardness	Muffins	5–10% grape pomace powder	Bender et al. (2017)
	Apple pomace powder (APP)	Drying and grinding	TDF = 62.67 ± 0.54%	↑Dietary fibers Improved physico-chemical properties	↑Hardness, ↓chewiness (sensory properties were not validated by a sensory analysis)	Buffalo meat sausages	APP = 2–8%	Younis et al. (2015)

TPC total phenolic content, *GPF* grape pomace flour, *GPP* grape pomace powder, *GP* grape pomace, *UAE* ultrasonic-assisted extraction, *GAE* gallic acid equivalents, *AGE* advanced glycation end product, *RGP* red grape pomace, *PLE* pressurized liquid extraction, *ESE* enhanced solvent extraction, *n/a* not available, *DGP* dried grape pomace, *TPI* total phenolic index, *TAnthC* total anthocyanidin content, *FNGP* Feteasca Neagra grape pomace, *GSM* grape skin phenolics encapsulated into maltodextrins, *C3G* cyanidin 3-glucoside, *AP* apple pomace, *WGPF* red wine grape pomace flour, *CAE* catechin equivalent, *TDF* total dietary fiber, *APP* apple pomace powder, *DW* dry weight

readily accepted that USN application increases yield by reducing the time and solvent consumption and is simultaneously recognized as environmentally friendly. Moreover, ultrasound technology can be implemented without difficulties in the existing equipment.

Local hotspots with high shear stress and temperature are created at the macroscopic scale as a result of ultrasonic application by cavitation bubbles. Cell walls were damaged and ruptured as a result of the development, growth, and collapse of microbubbles on the plant matrix's solid surface, allowing solvent to enter the cells and improving mass transfer (Khadhraoui et al. 2021).

Furthermore, according to Romani et al., ultrasound-assisted extraction (UAE) provided superior results when used at 55 °C, amplitude of 40%, and 6 min of treatment, compared to conventional extraction. With a total extraction volume of 200 mL, the extraction was carried out using water as the solvent in a ratio of 1:200 (g/mL). The higher antioxidant capacity showed an average extraction of 11% total phenolic compounds and 25% total anthocyanins (Bruno Romanini et al. 2021).

Pollini et al. (2021) reported UAE as the best extraction technique for polyphenolics from Red Delicious apple pomace. In this study, 50% ethanol with a solid to solvent 1:10 (g/mL) extraction was used at 60 °C for 60 min, resulting in a phenolic content of 1062.92 ± 59.80 μg GAE/g fresh apple pomace (Pollini et al. 2021).

14.4.2 Microwave

Additionally, microwave electromagnetic wave presents considerable performances in the extraction of bioactive compounds from various vegetal matrices, as a green solution, since it uses fewer resources and a variety of nontoxic solvents effectively. A lower extraction time is achieved by combining it with elevated temperature for the increase of the kinetic diffusion coefficients and reduction of the resistance to mass transfer (Da Rocha and Noreña 2020).

In microwave-assisted extraction (MAE), two oscillating electromagnetic fields with frequencies between 300 MHz and 300 GHz are used. Additionally, during MAE extraction by diffusion, the solvent permeates the solid matrix and dissolves the solute until it reaches a concentration that is constrained by the properties of the solid. In the final step, the solution contains the solute diffused to the surface naturally or by convection and diffusion (Angiolillo et al. 2015).

According to Álvarez et al., during a microwave pretreatment of 120 s, at a temperature of 100 °C and a power of 300 W, the polyphenol yield was increased by 57% and the anthocyanin one by a percentage of 17.6%. Also, these extracts' cellular bioactivity was increased by 83% and 133% (Álvarez et al. 2017).

Rocha and Noreña (2020) used an acidic aqueous solution with 2% citric acid as a solvent to separate the phenolic compounds using MAE and UAE. According to their results, both the total amount of phenolic compounds and antioxidant activity increased over time The best extraction condition corresponded to a microwave at

1000 W for 10 min, where, in contrast to the exhaustive extraction with methanol acidified solution, 45% of the anthocyanins were recovered (Rocha and Noreña 2020).

14.4.3 Pulsed Electric Field (PEF)

Due to its benefits in terms of efficiency and cost, PEF processing has a lower specific energy need and so offers a greener option. According to reports, the described approach is a revolutionary technology that can speed up by-product recovery while using less solvent and fewer heating stages (Arshad et al. 2020). As a result of the electroporation phenomenon, which causes the permeabilization of cell membranes, PEF treatment also promotes mass transfer (Brianceau et al. 2015). The charge accumulation on the membrane surfaces in response to an external electric field raises the transmembrane potential on both sides of the cell membrane. After crossing a crucial threshold of transmembrane potential, the growth of pores located in weak membrane regions causes a dramatic rise in permeability. In turn, this encourages the release of intracellular molecules (Barba et al. 2015).

As Brianceau et al. outlined in their study, PEF treatment at specific parameters—field strength $E = 1.2$ kV/cm, energy input $W = 18$ kJ/kg, and density $\rho = 1.0$ g/cm^3—increased the content of total polyphenols regardless of the extraction temperature. The ratio of anthocyanins to total flavan-3-ols at 20 °C rose from 7.1 to 9.0 compared to the control sample (Brianceau et al. 2015).

14.4.4 Thermal Treatment

Due to the selective character of the extraction procedures, the route from pomace to bioactive recovery is challenging. Thermal extraction methods include decoction, reflux, Soxhlet, hydro-, and steam distillation (Zhang et al. 2018). However, they are frequently limited by problems such as matrix overheating, loss of bioactivity, and poor product stability. Moreover, high energy consumption and overall expenses represent disadvantages, while the use of organic solvents may provide a challenge for the subsequent use of extracted compounds. In this regard, modern technologies may extract bioactive compounds at rates comparable to or superior to those achieved by conventional methods (Azmir et al. 2013). Material quantity is a major concern among the many elements that may influence technique selection (Monrad et al. 2014). For instance, polyphenol extraction using hot water is a simple procedure, but the quality of the pomace extract may be affected by high-temperature extraction (140 °C for 5 min) (Fernandes et al. 2019b). Anthocyanin and procyanidin extraction yields were highest from crude (wet) pomace compared to dehydrated or dried grape pomace (Monrad et al. 2012). Total recoverable polyphenol concentration, procyanidin components, tannin content, and antioxidant

activity of grape pomace and grape seed extract were not affected by 100 °C for 15, 30, and 60 min. However, for the same heat treatment, in grape seed extract, autoclave treatment resulted in significant hydrolysis of procyanidin B1 (75%), gallocatechin (70%), epicatechin (65%), catechin (61%), and procyanidin B2 (73%), and an increase in gallocatechin (100%), epicatechin gallate (129%), and gallic acid (71%) in grape pomace (Chamorro et al. 2011).

The initial step in developing further uses is to dehydrate wet pomace. Regarding total phenolic content, anthocyanin content, and DPPH antiradical scavenging activity, freeze-dried samples preserved the highest bioactive components, followed by ambient air-dried samples (Tseng and Zhao 2012). As shown, freeze-drying is not a viable approach for processing large volumes of wine pomace because of its slow rate of processing and more costly nature (four to eight times more expensive than traditional drying) (Garcia-Lomillo and Gonzalez-Sanjose 2017).

Ultimately, the most popular approach to get polysaccharides from grape cell walls is hot water extraction at 90 °C with a 1:10 solute:solvent ratio (Beres et al. 2016). Total polyphenol content in apple pomace decreased by 50% after hot water extraction (Fernandes et al. 2019a). On the other hand, the deterioration of polyphenolic compounds from grape pomace was reduced by using a semicontinuous extraction technique with heated solvent (water) in the extraction vessel maintained at ambient temperatures (Monrad et al. 2012). Raw samples of red grape pomace yielded 68% monomeric anthocyanins and 58% total flavonoids-3 (Monrad et al. 2014).

14.4.5 Enzymatic Treatment

The extraction of bioactive compounds utilizing enzymes relies on their capacity to disintegrate or disrupt the complex cell wall components, allowing stored substances to be released. The most common enzymes used for bioactive molecule extraction include cellulase, hemicellulase, protease, xylase, alcalase, polygalacturonase, α-amylase, neutrase, β-glucosidase, endopolygalacturonase, and pectinesterase (Sagar et al. 2018).

Grape skin cell walls are comprised of polysaccharides, acidic pectin compounds, lignin, and structural proteins linked together by ionic and covalent bonds (Meini et al. 2019). Therefore, many enzymes are required to decompose this complex matrix so that its constituent parts may be extracted (Teles et al. 2019). Higher anthocyanin extraction was achieved at the lowest temperature recorded (40 °C) and the proportion of enzymatic preparation (0.25%), producing a natural food colorant with a concentration of 2.67 g anthocyanin/100 g grape skin dry basis (Montibeller et al. 2019). Experiments were conducted to optimize the extraction procedure by determining the optimal combination of pretreatment, enzymatic hydrolysis time, solvent concentration, and distillation time. Maximum extraction efficiency was attained under conditions of 48 h of enzymatic hydrolysis, 70% ethanol concentration, and 20 min of distillation, emphasizing enzymatic hydrolysis (pectinase, α- and

β-glycosidase) as the best pretreatment technique (Liang et al. 2020). In the extraction of pectin in grape pomace, polygalacturonase, cellulase, xylase, and amylase were utilized. The total pectin content was 3.21–7.27% (Spinei and Oroian 2021). Enzyme-assisted extraction (xylanase, beta-glucanase, and cellulose) from apple pomace at 40 °C for 3 h provides 4.67–7.0% more pectin (Marić et al. 2018). To extract the soluble biomolecules from grape pomace, an enzymatic procedure was carried out using proteases (0.3% v/v) in a bioreactor using the pH-stat technique at 60 °C and pH 8 (Rodriguez-Morgado et al. 2015). Also, mono- and oligosaccharides from grape pomace can be extracted with enzymatic treatment and/or pretreatment by breaking glycosidic linkages from polysaccharide chains (Chamorro et al. 2012).

Apple pomace extracts, specifically the phenolic compound phlorizin, are the basis for a new class of oral antidiabetic and colon cancer medications. According to the results of one study, apple pomace might be used as a valuable ingredient in the development of novel drinks by providing a rich supply of natural bioactive components. Pectinase treatment at 20 °C/1 h was used for antioxidant extraction from apple pomace. The cloudy juice supplemented with pomace was rich in antioxidant phenolics, especially procyanidins, which proved to be particularly beneficial (in both extractable and non-extractable forms) (Oszmianski et al. 2011).

In comparison to existing procedures, enzymatic treatment of pomaces can increase polyphenol extraction yield and can be employed at low process temperatures, minimizing energy usage.

14.4.6 Pressurized Liquid Extraction

In comparison to atmospheric bioactive component extraction methods, pressurized liquid extraction (PLE) is superior due to its shorter extraction time, lower solvent consumption, and more control over the extraction's operating parameters (Huaman-Castilla et al. 2021). The most often utilized solvent for obtaining bioactive compounds are methanol-water or ethanol-water, limiting their food product applicability. However, the total phenolic content recovered from grape pomace by hot water extracted under pressure was very high (427 g GAE.mg^{-1}), with the majority of the phenols being anthocyanins and proanthocyanidins (Campos et al. 2021).

Because the solvent is pressured, PLE is effective at higher temperatures (beyond the boiling point of the solvent), which allows the solvent to stay in a liquid state, enhancing solvent characteristics and increasing the desorption and solubility of the desired molecules. High extraction temperatures (≥120 °C), on the other hand, destroy polyphenols, generating toxic chemicals and reducing sugar recovery. The polyphenol yields by water extraction using glycerol as a cosolvent were substantially greater than those from ethanol extraction using the same conditions. The extractability of phenolic acids was improved from 2.87 g/g (15%, 90 °C) to 98.53 g/g using a 50% water-glycerol combination at 150 °C (Huaman-Castilla et al. 2020).

A total phenol (up to 79 g GAeq/kg DW) was achieved by employing PLE, as a way to extract phenolic metabolites from grape pomace, although a limited variety of extracted compounds was recovered (polyphenols and flavonoids) (Ferri et al. 2020). The skin and seeds of grape pomace were subjected to hot pressurized liquid extraction at high temperatures (100–160 °C) using water-ethanol solvent combinations (20–60%). Phenolic acids were higher from seed (45.34 μg/g dw) than from bark (6.93 μg/g DW), being directly proportional to ethanol concentration and temperature. Flavonols were recovered only from the skin (17.53 μg/g DW) at 20% ethanol and the maximum temperature (160 °C) (Allcca-Alca et al. 2021).

14.4.7 Sub-/Supercritical Fluid Extraction

The technique of supercritical fluid extraction is known as supercritical CO_2 extraction, when CO_2 is employed as the only solvent. There are two major steps in this method: (1) solvent extraction of soluble compounds from a solid matrix using a supercritical fluid, followed by (2) expansion-induced separation of extracted components from the supercritical fluid (Fontana et al. 2013).

Moreover, CO_2 is not only nontoxic and suitable for use in food production, but it is also easily available, cheap, and of high quality (Valencia-Hernandez et al. 2021). Furthermore, the risk of deterioration is minimized since light and air are kept out of the extraction process. CO_2, on the other hand, is not a good solvent for polar polyphenols since it is nonpolar. The inclusion of organic cosolvents such as methanol, ethanol, and acetone improves CO_2 solvating power and polyphenol extraction yield (Massias et al. 2015). Due to methanol toxicity, greater cost, and environmental effect, ethanol was considered as an alternate activation and extraction/elution solvent (Da Silva et al. 2020). Using CO_2 and 25% moll cosolvent (ethanol at 96%), apple pomace was heated to 50 °C and subjected to 25 MPa pressure for 3 h to extract the phenols from apple pomace (catechin, procyanidin B1, epicatechin, and quercetin-3-glucoside) (Massias et al. 2015).

Subcritical water extraction is a potential biotechnological approach use in the isolation of biologically active substances from their natural environments that are also ecologically acceptable. Subcritical water, in particular, may affect solvent polarity and dielectric constant at high temperatures (170 °C) and pressures (10.70 MPa), with extraction time of 16 min resulting in enhanced procedures of extraction, improved mass transfer efficiency for extracts, and the preservation of biological activities, all of which have a high application potential (Zhang et al. 2020). Extraction above these circumstances resulted in the loss of the original composition of grape pomace owing to heat degradation reactions and the generation of Maillard metabolites; thus, 100 °C, 10.34 MPa, and 80 s were shown to be ideal for the recovery of phenolic compounds (Loarce et al. 2020). By using subcritical water for extraction, apple pomace pectin yield was 16.68%. The exothermic property of pectin was only impacted by its constituents and raw material, whereas

the endothermic property was impacted by the extraction temperature (Wang et al. 2014).

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Chapter 15
Secondary Metabolites and Antioxidant Activity of the Solid-State Fermentation in Fruit Waste/Bagasse

Diego Ibarra-Cantún, María Elena Ramos-Cassellis, and Marco Antonio Marín-Castro

Abstract The presence of secondary metabolites from fruit and vegetable residues in the agroindustry is an opportunity that the pharmaceutical, cosmetic, and food industries are taking to obtain compounds of biological interest that can be added to their products and provide added value. This is the case of phenolic compounds, which have demonstrated their antioxidant, anti-inflammatory, antiallergic, antiviral, anticancer, antimicrobial antimutagenic, and other properties. Solid-state fermentation is a method that has been used for the production of microbial secondary metabolites using solid or semisolid matrices as substrate; it is considered an economical technique, since it allows the development of microorganisms, the most widely used being filamentous fungi. Meanwhile, its bioavailability depends on the extraction method used, highlighting the nonconventional methods, which have been described as an environmentally friendly alternative to traditional methods that use significant amounts of solvents and energy. This chapter provides an overview of the importance of residues as biomass for obtaining microbial secondary metabolites, extraction methods, and their relevance in human food.

Keywords Antioxidant activity · Solid-state fermentation · Secondary metabolites · Residues · Waste

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15.1 Introduction

Globally, waste generation from agri-food industry activities is equivalent to one-third of the food produced for human consumption (FAO 2011, 2014). Waste management is a key component in achieving several of the United Nations Sustainable Development Goals set out in their 2030 agenda, which is to contribute to the sustainable and efficient use of natural resources (UN 2015).

Agroindustrial wastes, such as fruit bagasse, used for livestock feed, do not present any economic benefit, not to mention that most of these accumulate in open-air areas causing pollution problems to the environment. Most of the wastes generated in the agroindustry has lignocellulosic and lipidic characteristics. They contain high organic and nutrient loads, which pose a threat to both solid and water resources (Díaz-Vázquez et al. 2021).

These kinds of untreated wastes create various climate change-related problems by increasing the amount of greenhouse gases (Sadh et al. 2018a). Therefore, the management of this resource should promote the reuse of raw materials, the improvement of yields at the industrial level, and keep the generation of waste to a minimum (Chojnacka et al. 2021).

In recent years, agroindustrial wastes have been used as raw material for the generation of value-added products, a practice that currently prevails and is expected to continue in the future to reduce the environmental impact caused by them (Chilakamarry et al. 2022; Mejías-Brizuela et al. 2016). Solid-state fermentation (SSF) and submerged fermentation (SmF) are the two main types of bioprocesses employed in the production of secondary metabolites from agroindustrial wastes (Kumar et al. 2021; Martí-Quijal et al. 2021). Many authors have considered SSF the most appropriate technique since it implies lower amounts of water in the substrates, which requires less energy by producing less wastewater. Thus, SSF is believed to favor the environment more (Costa et al. 2018; de Castro et al. 2018). Conversely, SSF is excellent for the utilization of large amounts of wastes, such as husks, bagasse, seeds, hulls, corn residues, and so on (Almanaa et al. 2020). Recently, SSF has increased in popularity in the agri-food and pharmaceutical industries in terms of the production of enzymes, pharmaceuticals, agrochemicals, flavors, fragrances, colors, biopesticides, food additives made from organic acid, and secondary metabolites, among others (Jiang et al. 2020; Mondala 2015; Martins et al. 2011).

Secondary metabolites are organic molecules that do not perform essential functions for their growth and development but play an important role in the defense mechanisms of plants against various stress conditions due to being a diverse group of mostly natural products, including terpenes, phenolics, alkaloids, and glycosides (Isah 2019; Agostini-Costa et al. 2012). The production of secondary metabolites with antioxidant activity is part of the chemical protection of plants/fungi in their environment (Croteau et al. 2000).

SSF mimics the natural conditions of microorganisms (Thomas et al. 2013). Hence, the significance of optimizing parameters during SSF for the production of secondary metabolites by controlling factors in growth conditions, such as substrate

composition, humidity, temperature, light, and pH, among others (Manpreet et al. 2005).

Thus, this review aims to demonstrate the importance of solid-state fermentation, involving microorganisms for the production of microbial secondary metabolites with antioxidant activity from fruit wastes and by-products.

15.2 Solid-State Fermentation

Solid-state fermentation (SSF) is a biotechnological process that uses solid or semisolid matrices as substrates with the necessary amount of water for the growth and metabolism of microorganisms (Singh Nee Nigam and Pandey 2009).

The most important factors for proper fermentation are the inoculum volume of the microorganisms, humidity, temperature, pH, nutrient concentration, aeration, and particle size of the solid substrates (surface/volume ratio). In addition, one of the economic advantages of this technique is the inclusion of agroindustrial waste products as substrates since they provide the organic matter necessary for the growth and development of microorganisms (Vassileva et al. 2021).

Moisture content can affect microorganism growth as well as restrict oxygen diffusion between the substrates during fermentation (Pirota et al. 2013).

Londoño-Hernandez et al. (2020) consider pH and temperature as the most crucial factors to determine fermentation efficiency, and so optimization of these parameters is essential. The initial pH of the medium determines the adaptation, growth, and metabolic activity of the microorganisms used in SSF, as it affects the cell surface area and increases nutrient uptake (Germec and Turhan 2021). Most microorganisms prefer neutral and slightly acidic pH in the range of 4.5 and 6.5 for optimal biomass production. A pH value below 4 or above 7 slows fungal growth, whereas high temperatures facilitate the growth of biomass (Vassileva et al. 2021).

The substrate not only supplies nutrients to the microbial culture but also serves as an affix for the cells (Pandey et al. 2008). The most common solid substrates are lignocellulosic materials, such as straw, sawdust, or wood chips. Complex polymeric components, such as cellulose and hemicellulose make up wheat straw. Wood sawdust contains more recalcitrant compounds than wheat straw, mainly in the form of lignin (Fig. 15.1). Thus, both substrates require rot fungus to break down the lignified wood (Amini et al. 2022; van Kuijk et al. 2017).

However, in recent years, substrates of plant origin have been used, including cereal grains (rice, wheat, barley, and corn), legume seeds, wheat bran, and agroindustrial residues, like fruit peels from banana, orange, watermelon, pineapple, onion, potato, tomato, and sugarcane, which contain polymeric molecules that are concentrated sources of nutrients (Brito et al. 2020; Dessie et al. 2018; Ajila et al. 2012a). The high content of polysaccharides, such as cellulose, hemicellulose, lignin, proteins, enzymes, dietary fibers, fatty acids, flavors, smells, and bioactive compounds, present in this type of residue has led them to be considered as a substrate in SSF (Šelo et al. 2021; Ravindran et al. 2018; Sadh et al. 2018b). Since

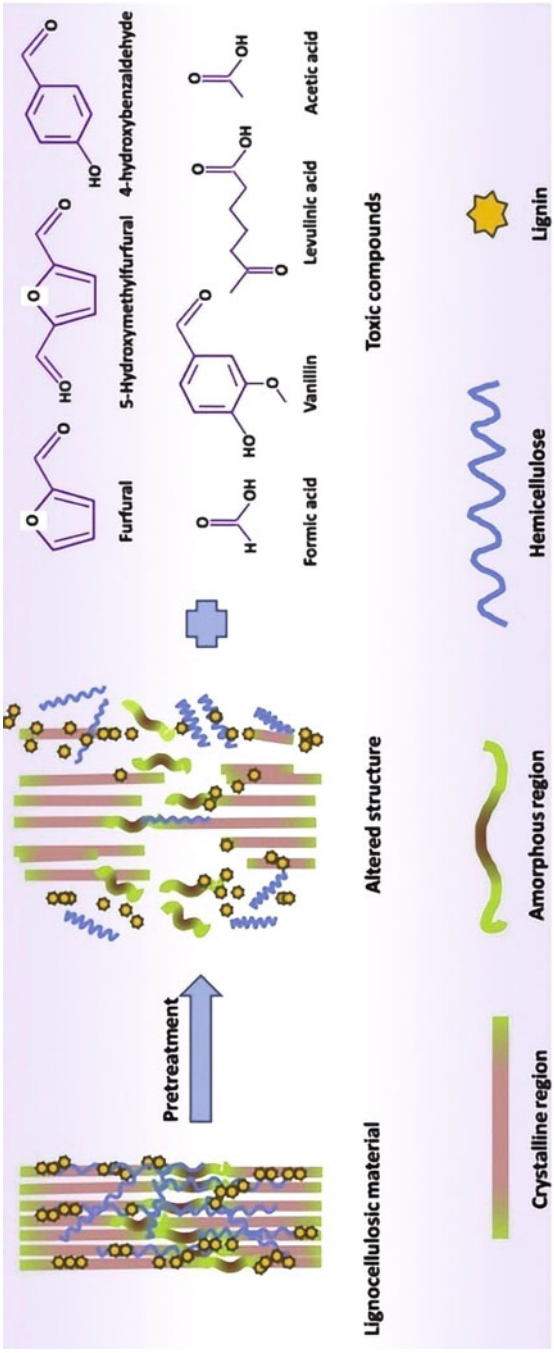

Fig. 15.1 Lignocellulosic biomass complex. (Source: Phitsuwan et al. 2013)

Fig. 15.2 Production of *Pleurotus ostreatus* (Jacq. ex Fr.) Kummer (**a**) in field, (**b**) collected, and (**c**) for consumption. (Source: own)

their lignocellulosic structure can be altered by the biocatalytic activities of different microorganisms, their chemical characterization is important in terms of establishing the optimal conditions for SSF (Šelo et al. 2021).

White-rot fungi include hundreds of basidiomycetes and some ascomycetes, which break down lignin, especially during the early colonization phase through accessing cellulose and hemicellulose and depolymerizing them at the fruiting stage (Stajić et al. 2016; van Kuijk et al. 2015). Species like *Phanerochaete chrysosporium*, *Ceriporiopsis subvermispora*, *Pleurotus eryngii*, *Pleurotus ostreatus*, *Lentinus edodes*, *Hericium clathroides*, and *Trametes versicolor* are used as inoculum during SSF (Knežević et al. 2013; Stajić et al. 2013, 2016; van Kuijk et al. 2015). As for ascomycetes, the most widely used ones in SSF are *Aspergillus niger*, *Aspergillus ibericus*, *Aspergillus oryzae*, and *Rhizopus oligosporus* (Feitosa et al. 2020; Vong et al. 2018; Oliveira et al. 2016; Murthy and Naidu 2010).

Yeasts and bacteria are also used in SSF (Lizardi-Jiménez and Hernández-Martínez 2017). Bacterial cellulose producing lactic acid bacteria, like *Bacillus* sp., *Streptococcus lactis*, *Leuconostoc*, *Bifidobacterium*, and *Acetobacter xylinum* (Rodríguez de Olmos et al. 2017; Zhang et al. 2014; Jung and Lee 2009), are also used in SSF (Weng and Chen 2010). Various yeasts have been used in SSF to improve the operating conditions and obtain a greater amount of compounds of biological interest. Shi et al. (2020) used *Saccharomyces cerevisiae* and *Hansenula* sp. with probiotics to improve the composition and quality attributes of okara. Martínez et al. (2017) used *Kluyveromyces marxianus* with a mixture of sugarcane bagasse and sugar beet molasses to obtain fruit-like aroma compounds. With that said, Mussatto et al. (2012) mention basidiomycetes as the microorganisms with the greatest potential for the production of compounds of biological interest through SSF. In the case of fruit residues, the proposed pretreatment of bagasse should first be physical, which involves grinding to generate different yields of fermentable sugars. This is then followed by biological treatment through SSF using the basidiomycete *Pleurotus ostreatus* that produces white wood rot (Fig. 15.2) (Wang et al. 2019).

15.3 Production of Microbial Secondary Metabolites of Biological Interest by FES

Microbial secondary metabolites (SMs) are the products of metabolism produced during the fermentation process and synthesized by microorganisms after the growth phase (Kumar et al. 2021).

In recent years, SMs have been widely used as anti-inflammatory, antitumor, anticancer, antioxidant, antidiabetic, antiviral, and antimutagenic agents in the pharmaceutical industry (Jain et al. 2019; Ghasemzadeh et al. 2015; Mohammed et al. 2014). As for the agricultural sector, they have been utilized as organic insecticides and pesticides (Zaynab et al. 2018; Adeyemi 2010). In the food industry, they have been included in flavorings, pigments, and surfactants (Cortés-Sánchez 2020; Ramalingam et al. 2019; Upadhyay 2018).

Environmental conditions, like light intensity, pH, humidity, oxygen, and nutrient content in the substrates, induce the production of SMs in a given ecosystem (Junior Letti et al. 2018; Krishna 2005). Thus, SSF can provide the natural environmental conditions for microorganisms, which is a crucial advantage in SM production. Since SSF-specific environmental stimuli have an effect on SM production, it is necessary to design better processes and detect potential targets (Barrios-González 2018).

The production of secondary metabolites through SSF helps the environment because it uses agroindustrial wastes as a source of phenolic compounds that have antioxidant, anti-inflammatory, antiallergic, antiviral, anticancer, antimicrobial, and antimutagenic properties (Leite et al. 2019; Sadh et al. 2018a; Martins et al. 2011; Robinson et al. 2001).

Most agroindustrial residues have lignin, which contains phenolic compounds, such as ferulic, *p*-coumaric, syringic, vanillic, and *p*-hydroxybenzoic acids (Panzella et al. 2020).

Phenolic compounds are compounds containing benzene rings with one or more hydroxyl substituents and range from simple phenolic molecules to highly polymerized compounds (Lin et al. 2016; Velderrain-Rodríguez et al. 2014). According to Agostini-Costa et al. (2012), their chemical structures may greatly vary between simple phenols (C_6), such as hydroxybenzoic acid derivatives and catechols, and long-chain polymers with high molecular weight, such as catechol melanins $(C_6)_6$, lignins $(C_6\text{-}C_3)_n$, and condensed tannins $(C_6\text{-}C_3\text{-}C_6)_n$. Stilbenes ($C_6\text{-}C_2\text{-}C_6$) and flavonoids ($C_6\text{-}C_3\text{-}C_6$) are phenolic compounds with an intermediate molecular weight that have many pharmacological and biological benefits.

While Surek and Nilufer-Erdil (2016) have reported significant amounts of phenolic compounds in pomegranate residues, Robledo et al. (2008) and Ajila et al. (2012b) have found higher amounts of phenolic compounds and antioxidant activity through SSF of pomegranate residues and apple pomace, utilizing *Aspergillus niger* and *Phanerochaete chrysosporium*.

During SSF, the lignocellulosic residues in conjunction with fungi release free phenolic compounds through enzymes (β-glucosidase), thereby improving the

functionality of these phytochemicals for health (Dulf et al. 2015; Ajila et al. 2012b). Mussatto et al. (2012) mention filamentous fungi as the most promising microorganisms of biological interest in terms of SSF. Table 15.1 shows some of the filamentous fungi used in SSF to obtain phenolic compounds.

15.4 Methods of Extraction of Secondary Metabolites of the Solid-State Fermentation in Fruit Waste

The interest in recovering phytochemicals from agricultural, forestry, and food industry residues aims at reducing the environmental impact of such wastes and improving sustainable economic growth. These phytochemicals can be employed widely in both food and feed, food supplements, and cosmetic products thanks to their various bioactivity properties (Rodríguez-Rojo 2021).

Secondary metabolites from plants and their residues have been obtained for decades through conventional extraction methods, such as Soxhlet and reflux, as well as infusion, decoction, digestion, maceration, and percolation (Wong-Paz et al. 2017; Devgun et al. 2012).

Conventional extraction processes are generally time-consuming. For example, maceration lasts 2–7 days and involves bulk amounts of organic solvents, resulting in damage or loss of antioxidant activity in the extracted compounds due to exposure to high temperatures for an extended period of time. The literature offers a number of practical examples for bioactive compound extraction using different Soxhlet extraction methods that require long extraction times and large quantities of solvents, including methanol, ethanol, *n*-hexane, petroleum ether, toluene, chloroform, benzene, diethyl ether, dichloromethane, acetone, isooctane, cyclohexane, isopropanol, and water (Hidalgo and Almajano 2017; Brglez Mojzer et al. 2016; Devgun et al., 2012).

Aramrueang et al. (2019), Wong-Paz et al. (2017), and Castro-López et al. (2016) mention that in the past decades alternative extraction technologies have been applied to obtain secondary metabolites due to the advantages they offered, such as simplicity, safety, and higher yields, compared to conventional extraction methods. Alternative extraction technologies include ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), enzyme-assisted extraction (EAE), supercritical fluid extraction (SFE), and pulsed electric field extraction (PEF). Table 15.2 lists the advantages and disadvantages of alternative extraction technologies in terms of secondary metabolites.

Martínez-Ávila et al. (2021) have concluded that these methods constitute viable alternatives from a technical economic point of view. Their advantages are numerous, including short extraction times, reduced costs, and reduced use of organic solvents that do not degrade the compounds or leave residues of toxic solvents, as well as increased yields, resulting in reduced environmental impact.

Table 15.1 Phenolic compounds with antioxidant activity produced by solid-state fermentation

Metabolite secondary	Microorganism	Residue	References
Phenolic compounds	*Aspergillus niger*	Apricot pomace	Dulf et al. (2017)
Flavonoids	*Rhizopus oligosporus*		
Polysaccharides	*Lentinus edodes*	Walnut shell	Reza et al. (2018)
Total, free phenolics	*Lentinus edodes*	Cranberry pomace	Zheng and Shetty (2000)
Phenolic content	*Lentinus edodes*	Cranberry pomace	Vattem and Shetty (2003)
Phenolic compounds	*Lentinus edodes*	Wine pomace	Yıldırım and Sözmen (2021)
Total, phenolic contents	*LAB*	Rice bran	Nisa et al. (2019)
	Lactobacillus lactic/Lactobacillus plantarum		
Polyphenols	*Aspergillus niger*	Pomegranate seeds and husk	Robledo et al. (2008)
Total, phenols	*Monascus purpureus*	Sea buckthorn seed residues	Zhang et al. (2019)
Flavonoids			
Phenolic compounds	*Ganoderma lucidum*	Brown and white teff	Gebru and Sbhatu (2020)
Total, flavonoids	*Pleurotus ostreatus*		
Total, phenolic content	*Trichoderma* spp.	Commercial turmeric	Mohamed et al. (2016)
Phenolic compounds	*Ganoderma lucidum*	Soybean residue	Yang et al. (2020)
	Lentinus edodes		
Polysaccharides	*Lentinus edodes*	Walnut shell	Reza et al. (2018)
Phenols	*Lentinus edodes*	Solid olive substrate	Lakhtar and Roussos (2016)
Protein	*Lentinus edodes*	Olive cake substrate	Vahidi et al. (2017)
Polyphenolics	*Phanerochaete chrysosporium*	Apple pomace	Ajila et al. (2012b)
Phenolic compounds	*Phanerochaete chrysosporium*	Apple pomace	Ajila et al. (2011a)
Phenolic content	*Phanerochaete chrysosporium*	Dried pistachio hulls	Abbasi et al. (2007)
Phenolic compounds	*Phanerochaete chrysosporium*	Larrea tridentata leaves	Martins et al. (2013)
Flavonoids			
Phenolic compounds	*Pleurotus sapidus*	Rice and sunflower side-streams	Pinela et al. (2020)
Phenolic contents	*Phlebia brevispora*	Wheat and paddy straw	Sharma and Arora (2014)
	Phlebia floridensis		
Phenols	*Pleurotus ostreatus*	Tomato pomace	Yaşar and Tosun (2020)
Tannins	*Phanerochaete chrysosporium*		

(continued)

Table 15.1 (continued)

Metabolite secondary	Microorganism	Residue	References
Phenolic content	*Trichoderma viride*	Ginger	Saleh et al. (2018)
Phenols	*Agaricus brasiliensis*	Residues	Mokochinski et al. (2015)
Flavonoids			

15.5 Health

Reactive oxygen species (ROS) have potentially harmful effects on both health and disease management (Lobo et al. 2010). Most of these effects are due to oxygen being given to other substances. These free radicals are highly reactive and capable of damaging biologically relevant molecules, like DNA, carbohydrates, proteins, nucleic acids, and lipids in the nucleus and in the membranes of cells (Mohammed et al. 2015). In other words, free radicals attack important macromolecules leading to cell damage and homeostatic disruption. Antioxidants delay or inhibit cellular damage due to their inhibiting oxidation of other molecules through giving an electron to a rampaging free radical and thereby neutralizing it (Neha et al. 2019; Lobo et al. 2010). Such antioxidants are found in fruits and vegetables in the form of vitamin C (ascorbic acid), B-carotene, and vitamin E (α-tocopherol) (Sonia et al. 2016).

Bioactive compounds have been shown to promote human health benefits, such as reducing the incidence of degenerative diseases like cancer (Ponte et al. 2021), type 2 diabetes (Lin et al. 2016), inflammatory processes involved in cardiovascular diseases (Serino and Salazar 2019; Ricordi et al. 2015), antimutagenic processes (Inami et al. 2017; Valdez-Morales et al. 2014), antiallergenic processes (Bessa et al. 2021), antifungal processes (Simonetti et al. 2020), antimicrobial processes (Elfalah et al. 2013), and antioxidant activity (Hernández-Carlos et al. 2019). These benefits for human health have reinforced research in fruits, vegetables, plants, and agricultural and agroindustrial residues to discover new sources of bioactive phenolic compounds. Clemente and Galli (2011) studied grape waste by extracting anthocyanins from industrially processed wine residues, whereas Martínez-Ávila et al. (2012) found that grape waste is a potential substrate source for the production of antioxidant compounds in SSF, mainly in the form of gallic acid. Carmo et al. (2018) reported that acerola residue (*Malpighia emarginata*) showed high amounts of bioactive compounds and polyphenols, both of which are high in dietary fiber, which is associated with antioxidant activity. Carvalho Gualberto et al. (2021) observed the presence of bioactive compounds and related antioxidant activities in the agroindustrial residues of acerola (*Malpighia emarginata* L.), guava (*Psidium guajava* L.), genipap (*Genipa americana* L.), and umbu (*Spondias tuberosa* L.) fruits.

Ajila et al. (2012b) studied the ability of *P. chrysosporium* to release phenolic antioxidants from apple pomace using SSF and concluded that SSF improved both the nutraceutical properties and antioxidant activity of apple pomace. Moreover,

Table 15.2 Advantages and disadvantages of alternative extraction methods for obtaining secondary metabolites

Method	Advantages	Disadvantages	References
Ultrasound-assisted extraction	High extraction efficiency	Lack of uniformity in the distribution of ultrasound energy	Ajila et al. (2011b)
	Reduced extraction time	Decline of power with time	Castro-López et al. (2016)
	Reduced solvent consumption		
	Good for thermolabile compounds		
	Simple to use		
	Little instrumental requirement		
Microwave-assisted extraction	High extraction efficiency	High capital cost	Ajila et al. (2011b)
	Reduced extraction time	Negative impact on thermolabile compounds associated with microwave heating	Castro-López et al. (2016)
	Reduced solvent consumption		Roselló-Soto et al. (2016)
	High extraction rate		
	High extraction yield		
Enzyme-assisted extraction	Low temperature	High cost of enzymes	Roselló-Soto et al. (2016)
	Reduced extraction time	Poor recyclability and reusability	Das et al. (2021)
	Little energy consumption	Degradation of enzymes under certain processing conditions	
	High extraction yield	Loss of catalytic activity after being used a certain number of times	
Supercritical fluid extraction	Reduced extraction time	High costs of infrastructure and operation	Ajila et al. (2011b)
	Eco-friendly method	High pressure requirement	Castro-López et al. (2016)
	Alternative to traditional organic liquid solvents		
	Good for thermolabile compounds		
	Highly purified extracts		
Pulsed-electric field	High extraction efficiency	High costs of infrastructure and operation	Castro-López et al. (2016)
	No loss of product quality due to nonthermal extraction	Relatively complicated process	Roselló-Soto et al. (2016)
	Selective extraction of metabolites		

Zambrano et al. (2018) studied phenolic antioxidants extracted from black grape (*Vitis vinifera* × (*Vitis labrusca* × *Vitis riparia*)), apple (*Malus domestica* cv. Jonagold), and yellow dragon fruit (*Hylocereus megalanthus*). Da Silva et al. (2021) extracted phenolic acids and flavonoids from apple pomace. Valdez-Morales et al. (2014) studied phenolic content as well as antioxidant and antimutagenic activity in the peel and seeds of different tomato types (grape, cherry, bola, and saladette). Phenolic compounds with important biological activities, like caffeic acid, ferulic acid, chlorogenic acids, quercetin-3-β-*O*-glycoside, and quercetin, were quantified.

15.6 Alimentation

In recent years, the consumption of fruits and vegetables has received more and more emphasis as a result of their potential health benefits due to the antioxidant potential of secondary metabolites contained in them. The specific defensive mechanisms taking place in fighting illnesses are associated with such antioxidants as vitamins A, C, and E as well as provitamins (Swallah et al. 2020). Recent studies indicate that plant polyphenolic compounds are the core phytochemicals exactly because of their antioxidant properties (Garcia-Salas et al. 2010). Phenolic compounds are the key determinants of the antioxidant potentials in plant foods (Kafkas et al. 2018).

Most of the reports confirm that regular consumption of fruits and vegetables contributes to a healthy diet and nonregular consumption could result in certain chronic diseases (Radavelli-bagatini et al. 2022; Wallace et al. 2020). Therefore, the consumption of at least five servings of vegetables, seeds, grains, legumes, roots, fruits, flowers, herbs, nuts, and leaves is recommended per day. The nutrients in plants have several benefits in terms of weight maintenance, proper development, satiety, and variety (Pinedo-Espinoza et al. 2020; Swallah et al. 2020; Oguntibeju et al. 2013).

The dietary intake of phenolics present in vegetables and fruits is influenced by the eating habits and preferences of the individual consumer (Shahidi 2004). The recommended intake of dietary polyphenols is 1 g per person, for which the main sources are fruits, vegetables, and legumes (Gulcin 2020; Scalbert and Williamson 2000). Shahidi and Ambigaipalan (2015) claim that phenolic antioxidants interfere with the oxidation process and act as free radical inhibitors and sometimes also as metal chelators. Additionally, it is shown that the risk of cancer decreases when an individual follows a diet rich in antioxidants rather than obtaining these compounds from dietary supplements (Aguilera et al. 2016; Pantavos et al. 2015).

Akhtar et al. (2019) mention fruits, flowers, seeds, and even the peel of pomegranate as a natural resource to treat microbiological and parasitic pathogenesis as well as inflammatory and infectious chronic ailments. Selmi et al. (2017) found that *Citrus sinensis* peel aqueous extract, as pretreatment, and its major flavonoid, hesperidin, protect against gastric ulcers induced by ethanol in rats. Salazar-López et al. (2021) studied the beneficial effects of phenolic compounds and the antioxidant

capacity of the indigestible fraction of avocado peel and the enzymatic processes involved in the gastrointestinal system in vitro.

Therefore, the fortification of food products with antioxidant compounds, residues with high amounts of dietary fiber, and polyphenolic compounds can enhance the nutritional value and help in disease prevention, not to mention that it positively affects the stability as well as organoleptic and technological properties of the final product (Subiria-Cueto et al. 2022; Zehiroglu and Ozturk Sarikaya 2019).

15.7 Functional Foods

Functional foods have a positive effect on health, exceeding the expectations of basic nutrition. In general, functional foods are food sources that in addition to their nutritional value have one or more biologically active components that provide added benefits in terms of maintaining one's health and reducing the risk of certain diseases (Beltran 2016).

First, Valdez-Morales et al. (2014) worked with residues from peels and seeds of tomato produced in an industry that favors intensity in color and sweetness and demonstrated that tomato by-products improved some sensory properties. However, when conditioning treatments, such as blanching and peeling are carried out, in addition to phenolic compounds, lycopene β-carotene and ascorbic acid decrease too, making it necessary to have alternatives to help maintain and recover them.

Second, Ajila et al. (2011a) mention that the economic value of agroindustrial wastes could easily be increased by pretreatment with fungi through SSF prior to the recovery of valuable hydrophilic and lipophilic components. An example of this would be "manzarin," a feedstuff for animal consumption produced through SSF, the nutritional value of which is higher than apple bagasse, containing less of the constituents of the cell wall, which makes it more easily digestible. In addition, it has been proven that the fermentation process produces considerable amounts of organic acids (acetic, propionic, butyric, and lactic) (Ajila et al. 2012a), which can be used as preservatives in foods and beverages as they can prevent spoilage and prolong shelf-life. Similarly, it has been shown that fermentation significantly improves both the nutritional composition and antioxidant content, as well as contributes to the sensory properties of foods. A representative example is okara, or soybean paste, in which a total of 154 mg of gallic acid, equivalent to 100 g of dry sample, and important aromatic substances were found (Shi et al. 2020).

15.8 Conclusions

It is important to consider the technologies for the use, reuse, and value addition of residues because they can be related to environmental pollution caused by pesticides, herbicides, fertilizers, and synthetic agrochemicals in intensive agriculture.

Detecting and reporting the presence of these agricultural pollutants in agroindustrial residues is essential for their proper treatment. Solid-state fermentation is an alternative method that favors the valorization of lignocellulosic biomass produced in the agri-food industry, which has beneficial effects on both the quality and quantity of secondary metabolites. SSF can also contribute to the generation of products with higher nutritional content and disposition through cleaner technologies with greater energy savings and fewer resources, thus moving towards sustainable development.

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Chapter 16
Green Extraction Techniques Applied to Recover Chemical Compounds from Olive-Derived Biomasses

María del Mar Contreras, Irene Gómez-Cruz, Ángel Galán-Martín, Inmaculada Romero, and Eulogio Castro

Abstract Extra-virgin olive oil is a high-quality product from the Mediterranean basin. Its production is associated with the generation a huge quantity of biomasses. These biomasses contain interesting bioactive compounds such as mannitol, phenolic compounds like hydroxytyrosol and oleuropein, and triterpenic acids. This chapter first gives an overview of these biomasses generated from the field to the pomace olive oil extracting industries. Then, green extraction technologies are reviewed and examples of application to recover the aforementioned bioactive compounds are shown. Most studies have been carried out at laboratory scale, and thus, the potential deployment of these technologies to extract bioactive compound from olive-derived biomasses is also discussed.

Keywords Green extraction · Microwave · Phenolic compounds · Ultrasound · Supercritical CO_2

16.1 Introduction

Olive oil is a significant agroindustrial product in the Mediterranean basin. Spain, Greece, Italy, and Portugal are the major producer countries, with about 50%, 9%, 8%, and 3% of the world production, respectively, along with other Mediterranean countries (FAO 2019; International Olive Oil Council 2020). The current olive grove surface is about 12.8 million ha and the olive oil production was about 3.1 million metric tons in 2019 based on the FAOSTAT last data (FAO 2019). As an example, Fig. 16.1 shows the large surface dedicated to olive grove cultivation in the Mediterranean basin. Therefore, the olive farming and olive oil mills are concentrated in

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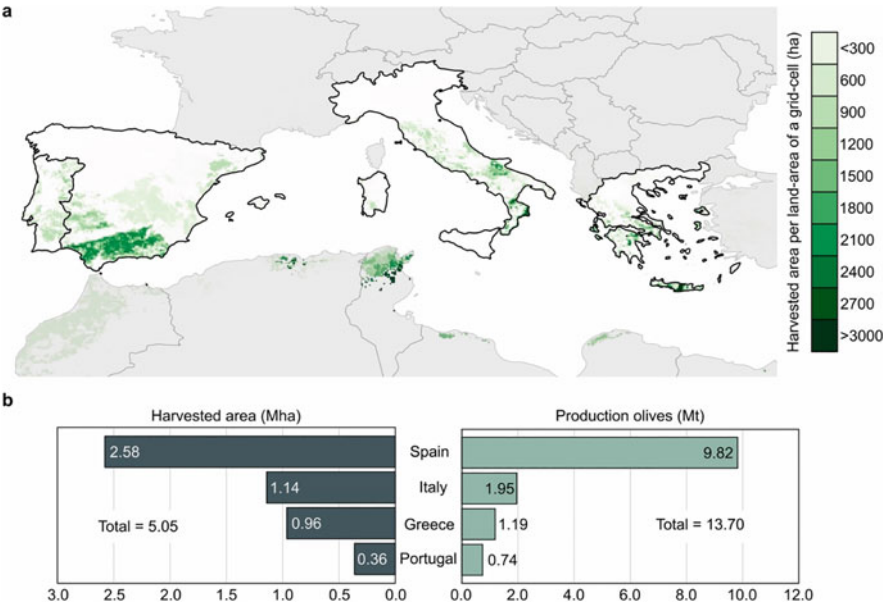


Fig. 16.1 (**a**) Distribution of the olive groves, (**b**) harvested area, and olive production in the major EU producers. (Reprinted from Renewable and Sustainable Energy Reviews, 165, (Galán-Martín et al. 2022) 112609, Copyright (2022), with permission from Elsevier)

this region (Gullón et al. 2020) and generate a series of biomasses including the following (Fig. 16.2):

- Olive tree pruning (OTP): OTP is produced in the olive farms each year to remove unproductive branches and facilitate the collection of fruit during the next crop (Manzanares et al. 2017; Contreras et al. 2020a). In a dry basis, it consists of over 25 wt% leaves, 50 wt% thin branches, and 25 wt% wood (Manzanares et al. 2017). Thick wood (>5 cm, diameter) is usually separated and used for domestic heating (Gullón et al. 2018).
- Olive mill leaves (OML): when the olives are not collected by handpicking, they are generally transported with OML to the olive mill. This biomass contains leaves and small thin branches (<0.5 cm) and it is separated from the collected olives as a result of the cleaning operations previous to the milling of the olives for olive oil extraction (Gullón et al. 2018; Contreras et al. 2020a; Doménech et al. 2021).
- Olive pomace (or olive cake or husk) (OP): OP is the main by-product generated in the mills. After cleaning, olives are ground, and then the paste is malaxed and the oil separated from the OP by discontinuous pressing (traditional mode) or continuous centrifugation (two- and three-phase extraction). Besides olive oil and OP, in the traditional and three-phase extraction modes, a brownish/black wastewater (or "alpechín") is also separated due to some amount of water added during the processing (Gullón et al. 2020).

Fig. 16.2 Olive-derived biomasses generated in the olive oil production chain

Therefore, OP consists of a semisolid or sludge whose moisture and residual oil content will mainly depend on the olive oil separation process. For example, a drier OP is obtained using pressing and three-phase decanters than using the two-phase decanters (Toscano and Montemurro 2012; Galán-Martín et al. 2022). OP can represent 80 wt% (or higher) of the processed olives, depending on the processing type and olive cultivar. It is comprised of olive skin, pulp, pits, and residual oil (Manzanares et al. 2017; Talhaoui et al. 2015).

In Spain and other countries, OP is partially destoned, dried, and granulated to extract the residual oil by hexane (Moral and Méndez 2006) which after chemical refining is named pomace olive oil (Manzanares et al. 2017, 2020). From these operations, a large part of the olive pits (or olive stones, OS) contained in the OP is generally separated before oil extraction (Doménech et al. 2021). For destoning, industrial pitting machines are applied with ~6-mm sieve separators (Lama-Muñoz et al. 2014). In addition, the exhausted olive pomace (EOP) (dried, deoiled or extracted olive pomace, "orujillo") is generated with a low moisture content (~10%) and it contains residues of the olive fruit pulp, seeds, skins, and stones. It is generally burnt to locally produce heat and/or electricity. Moreover, another current practice is the cleaning of the collected OS fraction to increase its energetic value, generating a residual pulp (or residual fraction from olive pits cleaning, RFOPC). This by-product is rich in, mainly, olive skin and pulp (Contreras et al. 2020a, b).

This chapter will focus on the aforementioned olive-derived biomasses, which are summarized in Fig. 16.2, considering those generated from the farm to the pomace olive oil production, i.e., OTP, OML, OP, EOP, OS, and residual pulp.

Other processing approaches are marginally performed in some olive mills, for example, destoning the olive fruit prior to milling and olive oil extraction, while

others have introduced the multiphase decanter (Contreras et al. 2020a; Durante et al. 2020; Criado-Navarro et al. 2021). Both practices will lead to OP with different characteristics (Padalino et al. 2018; Durante et al. 2020).

Olive-derived biomasses are characterized by the presence of a high content of extractives, which consist of nonstructural compounds (e.g., inorganic cations and anions, nitrogenous components, organic acids, nonstructural carbohydrates, polyalcohols, phytochemicals, chlorophyll, waxes, etc.) (Sluiter et al. 2005; Doménech et al. 2021; Gómez-Cruz et al. 2021b). This fraction is interesting since it contains a wide range of extractable valuable compounds such as bioactive compounds that can be applied in different sectors (Contreras et al. 2020a; Doménech et al. 2021). As a first valorization step of these olive-derived biomasses, these compounds can be extracted that otherwise will be lost. The extraction of these high value-added chemicals can be a source of new incomes to the sector and it favors their usefulness for combustion (gasification or pyrolysis) and sugar recovery and conversion in a multiproduct biorefinery platform to also produce high value-added chemicals (e.g., biofuels) (Galán-Martín et al. 2022). This is another important issue towards the transition to a sustainable circular economy in the Mediterranean basin, where these biomasses are mainly produced, and also to be aligned with the sustainable development goals (SDG) of the UN's Agenda 2030.

Accordingly, the extraction of these chemicals from these biomasses has gained increased attention and numerous studies have evaluated "green" technologies for this purpose to achieve more sustainable processes to meet UN's SDG goals. This chapter will overview these technologies applied to recover extractable value-added compounds from olive-derived biomasses.

16.2 Extractive Fraction of Olive-Derived Biomasses and Extractable Bioactive Compounds

The extractive fraction refers to a mixture of nonstructural components in biomass. This term was defined by the National Renewable Energy Laboratory (NREL) of the United States to chemically characterize lignocellulosic biomasses (Sluiter et al. 2008; Doménech et al. 2021) like olive-derived biomasses. According to the NREL, extractives can be either aqueous or organic, depending on whether they are extracted with water or with an organic solvent such as ethanol using Soxhlet extraction (Sluiter et al. 2008; Doménech et al. 2021). The total content of extractives in olive-derived biomasses mainly depends on the by-product type (Fig. 16.3). According to this figure, the values vary about 6 wt% for OS and 53 wt% for EOP on a dry basis (Miranda et al. 2019; Contreras et al. 2020a; Doménech et al. 2021).

This fraction can be divided in aqueous extractives and ethanolic extractives based mainly on their polarity, as commented before. In the residual pulp, the extractive fraction has more apolar features (68% are ethanolic extractives), while in OL, OTP, OML, and EOP contain more polar compounds (>60% are aqueous extractives) (Fig. 16.3). This preliminary characterization gives an idea of the

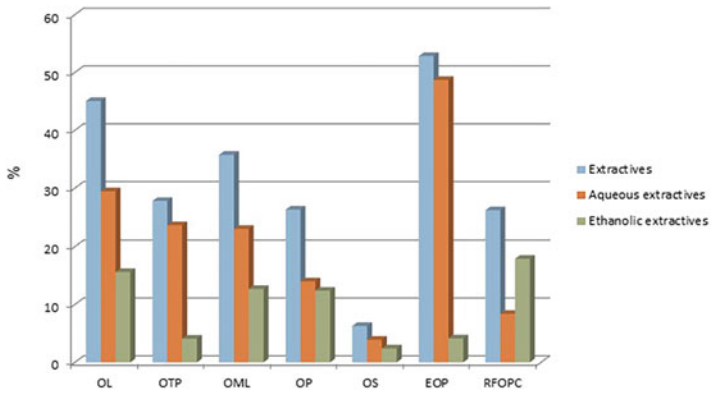


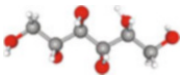
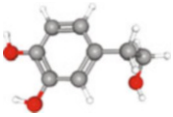
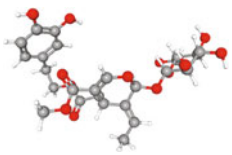
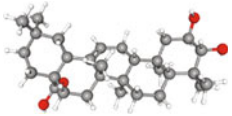
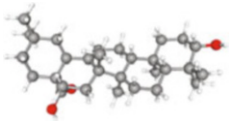
Fig. 16.3 Content of extractable compounds in olive-derived biomasses: olive leaves (OL), olive tree pruning (OTP), olive mill leaves (OML), OP (olive pomace), olive pits (OS), exhausted olive pomace (EOP), and the residual pulp (RFOPC). (Based on Miranda et al. 2019, Contreras et al. 2020a, Doménech et al. 2021)

richness in extractable components of these biomasses. Their partition by the extraction process and subsequent characterization will give insight into the bioactive compounds extracted and their richness. In fact, the extractive fraction is highly complex and its composition varies in function of the biomass considered and the olive cultivar (Contreras et al. 2020a, 2021; Lama-Muñoz et al. 2020; Medfai et al. 2020). Among these compounds, the presence of polar bioactive compounds such as mannitol and hydroxytyrosol and compounds with lower polarity like oleuropein and triterpenic acids, including oleanolic acid and maslinic acid, is remarkable (Contreras et al. 2020a). These compounds have pharmacological properties and functional properties (e.g., antioxidant activity) that can be used in the food, pharmaceutical, feed, and cosmetic industries (Lozano-Mena et al. 2014; Contreras et al. 2020a; Gullón et al. 2020). As an example, Table 16.1 shows some bioactivities of these compounds proved in clinical trials. Other bioactive compounds that could be found in some of these biomasses are squalene, phytosterols, and tocopherols (Otero et al. 2021).

16.3 Green Extraction Technologies Applied to Recover Bioactive Compounds from Olive-Derived Biomasses: General Aspects

The extraction of bioactive compounds from olive-derived biomasses is primally performed by solid-liquid extraction (leaching or lixiviation), whose basic mechanisms consist of penetration of the extraction agent or solvent in the biomass matrix, the diffusivity of compounds of interest to the outer space, and the solubility of these

Table 16.1 Example of pharmacological properties reported in clinical trials and uses of bioactive compounds found in olive-derived biomasses

Compound	Class	Bioactivity	References
Mannitol 	Polyol	Reduction of elevated intraocular and intracranial pressure	Vademecum (2020), Martău et al. (2020)
		Promotion of diuresis	
		Sweetener	
Hydroxytyrosol 	Phenolic compound	Antioxidant	Nobili et al. (2019), Knaub et al. (2020), Ramirez-Tortosa et al. (2019)
		Improvement of steatosis in children (combined with vitamin E)	
		LDL-cholesterol-lowering effect	
		Improvement of the prognosis of patients with breast cancer (combined with epirubicin plus cyclophosphamide)	
Oleuropein 	Phenolic compound	Antioxidant	El-Gogary et al. (2021), Carnevale et al. (2018)
		Decrease of psoriatic manifestations	
		Improving postprandial glycemic profile	
Maslinic acid 	Triterpenic acid	Prevention of the mobility-related disability in elderly persons (combined with moderate resistance training)	Nagai et al. (2019), Fukumitsu et al. (2016)
		Alleviating mild knee joint pain and having anti-inflammation effects	
Oleanolic acid 	Triterpenic acid	Reduction of the risk of developing diabetes in prediabetic patients (in enriched olive oil)	Santos-Lozano et al. (2019)

compounds in the solvent (Priego-Capote 2021). Conventional extraction of natural valuable compounds includes Soxhlet extraction, hydrodistillation, heat-reflux extraction, and maceration (Mandal and Mandal 2010; Gullón et al. 2020). In the former cases, the extraction efficiency is high, but these methods use large volumes of organic solvents and prolonged extraction times, being high-energy-demand technologies (Lama-Muñoz et al. 2020). It can also lead to thermal degradation of thermolabile molecules and poor product quality when high temperatures are

required for extraction (Ying et al. 2014; Durante et al. 2020) which is related to the boiling temperature of the solvent (Priego-Capote 2021). Alternatively, maceration can be applied at room temperature, but it also requires long extraction times (hours to days) (Mandal and Mandal 2010; Priego-Capote 2021). Maceration can be assisted by heat to improve the extraction efficiency or reduce the extraction time (Alu'datt et al. 2010; Ghanem et al. 2019), but again thermal degradation should be controlled. In general, the basic equipment to perform these processes is not expensive (Priego-Capote 2021).

Today, there is an interest in the application of "green" technologies to face the aforementioned limitations but without compromising the extraction yields. This includes the use of ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), supercritical CO_2 extraction (SCE), pressurized liquid extraction (PLE), and electro-based extraction, among others. Some of them, such as UAE, SCE, and electro-based extraction, are also known as cold extraction techniques, because the temperature during the extraction process is quite low compared to other techniques. Thus, the stability of those thermolabile compounds is barely affected (Tiwari 2015).

Additionally, the use of organic solvents rises concerns of health safety and environmental pollution, especially those highly toxic like methanol or coming from fossil resources like *n*-hexane and acetone. In this context, to recover bioactive compounds, the use of water, ethanol, and natural deep eutectic solvents (NADESs) is also attracting interest. Water is a low-cost and nontoxic solvent, while the others can be obtained from natural resources (Durante et al. 2020; Gullón et al. 2020). Therefore, the combination of these solvents and green technologies for the extraction of natural bioactive compounds from olive-derived biomasses is of utmost interest to move towards the circular bioeconomy and to meet the SDG principles.

There are some general aspects that have to be considered when optimizing these technologies since it can have an impact in the solubility, mass transfer, and stability of the bioactive compounds: the moisture; particle size; the temperature, especially in MAE and SWE; pH; and extraction time (Roselló-Soto et al. 2015; Soto-García and Rosales-Castro 2016; Zhang et al. 2018; Lama-Muñoz et al. 2019a; Taamalli et al. 2020). The solvent polarity will also affect the content of total soluble compounds extracted, the extraction yield, the compounds recovered, and so their richness, which will be determined by their chemical structure (Guntero et al. 2015). Table 16.2 shows some physicochemical properties of bioactive compounds found in olive-derived biomasses. For example, mannitol, hydroxytyrosol, and its derivatives can be extracted with aqueous-alcohol solutions, while pure or almost pure alcohols and supercritical CO_2 can be applied to recover triterpenic acids (Durante et al. 2020; Gómez-Cruz et al. 2021b). Sometimes, co-extraction of phenolic compounds and triterpenes occurs (Xie et al. 2019; Contreras et al. 2020a; Taamalli et al. 2020). In addition, phenolic compound can be found in free form and linked to the polymeric matrix, which requires alkaline and acid hydrolysis for their recovery. As an example, Alu'datt et al. (2010) have found that bound phenolic compounds could occupy over 33% of the total content of phenolic compounds in defatted olive

Table 16.2 Some characteristics of olive-derived bioactive compounds retrieved from PubChem and HMBD

Compound	Molecular weight (Da)	Molecular formula	Hydrogen bond donor count	Hydrogen bond acceptor count	Solubility in water (g/L)	Boiling point (° C)	LogP	pK_a
Mannitol	182.17	$C_6H_{14}O_6$	6	6	216 (at 25 °C)	290–295 (at 3.5 mm Hg)	−3.1[a], −2.7[b], −3.7[b]	12.59[c], −3[d]
Hydroxytyrosol	154.16	$C_8H_{10}O_3$	3	3	271.6 (at 25 °C)	355 (at 760 mm Hg)	0.02[a], 0.13[b], 0.89[b]	9.45[c], −2.4[d]
Oleuropein	540.52	$C_{25}H_{32}O_{13}$	11	6	1.734 (at 25 °C)	773 (at 760 mm Hg)	0.11[b], 0.63[b]	9.28[c], −3[d]
Maslinic acid	472.71	$C_{30}H_{48}O_4$	4	3	0.000004 (at 25 °C)	570 (at 760 mm Hg)	7.87[a], 6.06[b], 5.52[b]	4.74[c], −3.2[d]
Oleanolic acid	456.711	$C_{30}H_{48}O_3$	3	2	0.0000017 (at 25 °C)	553–554 (at 760 mm Hg)	8.58[a], 7.09[b], 6.59[b]	4.74[c], −0.84[d]

[a] Experimental value
[b] Predicted value
[c] pK_a (strongest acidic)
[d] pK_a (strongest basic)

Table 16.3 Specific parameters to be optimized when using green extraction technologies: Ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), supercritical CO_2 extraction (SCE), and high-voltage electric discharge (HVED)

Characteristic operating parameter	UAE	MAE	PLE	SCE	HVED
Amplitude	×				
Time	×	×	×	×	×
Temperature	×	×	×	×	
Pressure		×[a]	×	×	
Energy power	×	×			×
Frequency	×	×			
Modifier (or cosolvent) addition				×	
Pulse duration					×

[a] Only on closed-vessel mode

stones. In two-phase olive pomace, bound phenolic compounds were in smaller proportion (10–25%) of the total content of phenolic compounds.

Other crucial parameters to be studied will depend on the technology applied, which are summarized in Table 16.3. How these parameters affect the extraction of bioactive compounds will be detailed in the following section.

The effect of these operating parameters on the extraction yield of bioactive compounds could not give a linear answer and so kinetic studies, response surface methodology (RSM) with polynomial regressions, and artificial neural network (ANN) could be applied in the optimization. RSM and ANN are statistical approaches that enable to determine the most critical factors affecting the extraction process and the optimization of the operating conditions (Said et al. 2020). RSM can also be useful to evaluate how the interaction of the evaluated factors affects the content of bioactive compounds extracted (Gómez-Cruz et al. 2020). However, the optimal operating conditions will ultimately depend on the bioactive compound. So, when several bioactive compounds are extracted, the conditions can be selected in the function of the yield of the most interesting one or, as a compromise, a desirability function can be applied to simultaneously maximize all responses (Roselló-Soto et al. 2015; Gómez-Cruz et al. 2021b).

16.4 Theory and Application of Green Technologies to Extract Bioactive Compounds from Olive-Derived Biomasses

16.4.1 Ultrasound-Assisted Extraction

UAE is based on the incidence of ultrasonic waves with a frequency ranging from 20 to 100 kHz (<1 W/cm^2) (Osorio-Tobón 2020). This technology provides high shear forces in the solvent to promote extraction (Contreras et al. 2019). It is the

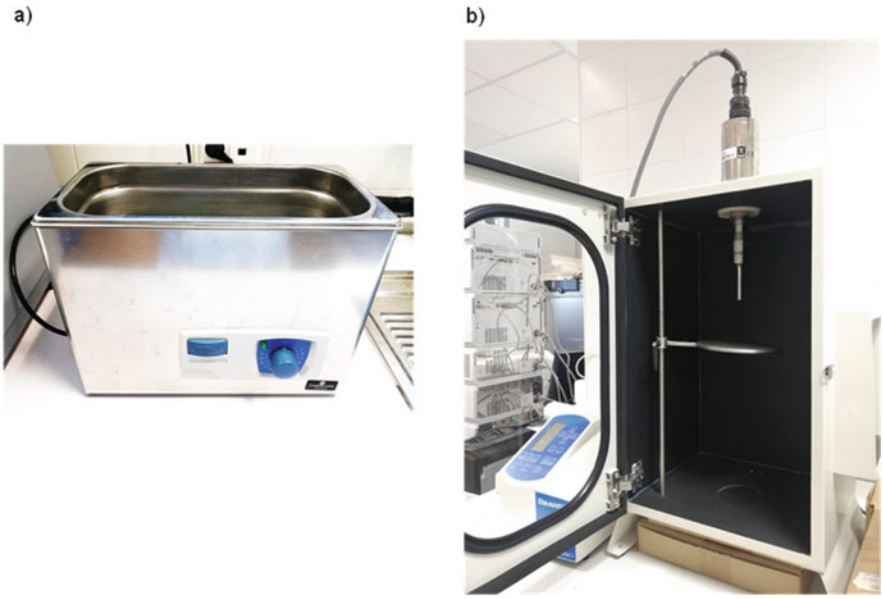


Fig. 16.4 Images of (**a**) bath- and (**b**) probe-type ultrasounds from JP Selecta and Branson, respectively

result of the acoustic or ultrasonic cavitation, although the cavitation threshold depends on the frequency (Zhang et al. 2017). This phenomenon also depends on the intensity, temperature, and viscosity of the medium (Panda and Manickam 2019). When waves propagate through a medium, a series of compressions and expansions occurs in the molecules of the medium. Each change in pressure causes the formation, expansion, and collapse of the bubbles formed, finally leading to the implosion of the bubbles in the solvent during the compression phase (Lavilla and Bendicho 2017). It produces high temperature and pressure appearing in the local area (Zhang et al. 2017). This phenomenon is responsible for the disruption of cell walls, promoting the accessibility between the solvent and the matrix and, as a consequence, an improvement in the mass transfer (Xu et al. 2017).

Ultrasonic extraction is affected by various factors such as frequency, temperature, extraction time, amplitude, intensity, sonication power, and properties of the solvent used (Chemat et al. 2017). Although it is considered a nonthermal extraction technique, if temperature is not controlled, it can reach relatively high temperatures at the end of the extraction depending on the conditions applied (Gómez-Cruz et al. 2021a).

At laboratory scale, the devices commonly used for the extraction of bioactive compounds are the ultrasonic bath and probe-type ultrasound (Martínez-Patiño et al. 2019). The former generally has lower intensity since the transducer is not in contact with the sample, while in the probe-type system (Fig. 16.4), the energy is applied directly to the sample, so the energy loss is negligible (Wen et al. 2020).

In UAE, the ultrasonic intensity, amplitude, and temperature are crucial parameters to be optimized (Xie et al. 2019; Gómez-Cruz et al. 2021a). The effect of these factors on the extraction of bioactive compounds should be considered together with the effect of the extraction time. Amplitude is related to the maximum height of a sound wave and so to the intensity (Gómez-Cruz et al. 2021a). At the same time, intensity and power are related through $I = P/(\pi r^2)$ (Xie et al. 2019). Temperature can be controlled or not. That is, if it is not regulated, the increase of temperature is related to the increase of the sonication time in the ultrasonic. In the case of the probe-type ultrasound, the temperature increases are related to the application of both longer sonication times and higher amplitude percentage (Gómez-Cruz et al. 2021a). In any case, the effects of these parameters and the optimum conditions will depend on the bioactive compound type (Xie et al. 2019; Gómez-Cruz et al. 2021a, b). The choice of the working temperature range is important to avoid the degradation of the olive bioactive compounds (Meullemiestre et al. 2016), but it depends on the other parameters and the thermal stability of each compound. The sonication time usually shows a marked quadratic effect (Meullemiestre et al. 2016; Gómez-Cruz et al. 2021b) but it depends on the studied domain (Gómez-Cruz et al. 2021a). This means that although this parameter favors diffusion, longer extraction times can promote decomposition, which could be related to the temperature increase or the results in the formation of much higher levels of free radicals in the liquid that lead to a higher degradation rate (Meullemiestre et al. 2016; Gómez-Cruz et al. 2021b).

16.4.2 Microwave-Assisted Extraction

This technology uses electromagnetic waves of frequency in the range from 300 MHz to 300 GHz. The most common microwave operates at 2.45 GHz (Contreras et al. 2019). It is able to disrupt hydrogen bonds and increase the porosity of the biomass matrix (Contreras et al. 2019), improving the penetration of the solvent into the matrix and facilitating the extraction of compounds. Microwave radiation is able to heat a matrix externally and internally without the need for a thermal gradient (de la Calle and Costas-Rodríguez 2017). This allows to shorten the extraction time, energy consumption, and solvent requirement (Nabet et al. 2019). Compared with conventional heating, MAE also provides a more effective heating, faster energy transfer, and lower solvent requirement (Contreras et al. 2019).

MAE can be classified according to whether the equipment is open or closed (Yahya et al. 2018) (Fig. 16.5). Both closed vessel and open types are commercially available as multimode and monomode (or single mode). In the first case, there is a random dispersion of microwave radiation inside the cavity of the equipment, so that all areas of the cavity and the sample are irradiated uniformly (Delazar et al. 2012). This can be used to perform multiple extractions in parallel. Alternatively, single-mode microwaves have a small cavity in which microwave irradiation is focused directly onto a single vessel (Anton Paar 2021) (Figs. 16.5 and 16.6).

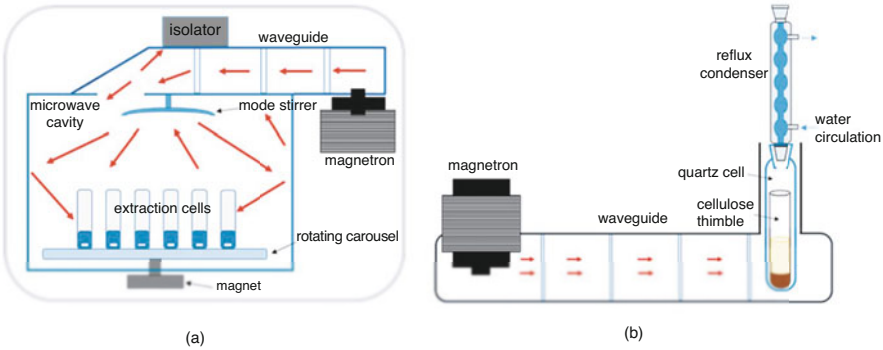


Fig. 16.5 Scheme of (**a**) pressurized and multimode microwave reactor and (**b**) atmospheric pressure and monomode microwave reactor (Moret et al. 2019)

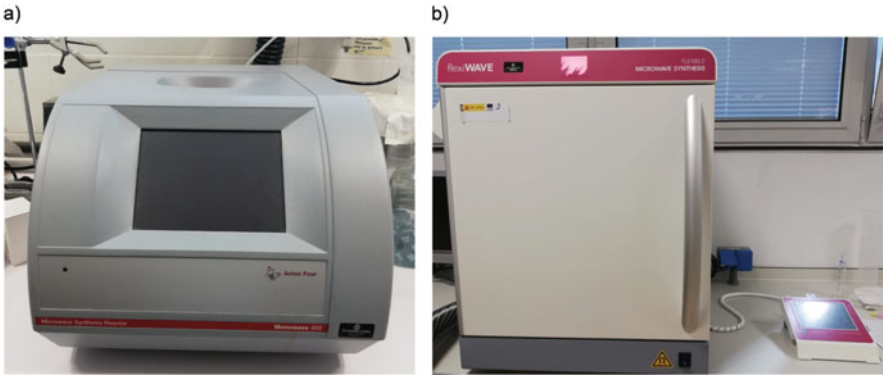


Fig. 16.6 Images of (**a**) monomode and (**b**) multimode microwave from Anton Paar and Milestone, respectively

The choice of the solvent and the optimization of the operating parameters—temperature, power, and extraction time—are crucial for obtaining high yields of bioactive compounds by this technology (Xie et al. 2019). The extraction solvent should be able to absorb microwave energy, so that the extraction becomes possible; for example, polar solvents like ethanol and water absorb microwave radiation, while the extraction with nonpolar solvents is not effective. Solvents can be characterized in terms of the loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$), which indicates the capacity to transform the absorbed energy into heat. So, a good absorber should have $\tan \delta \geq 0.1$. A high loss factor (ε'') at the microwave frequency applied will heat at a faster rate (Ibrahim and Zaini 2017). Table 16.4 shows these parameters for some common solvents applied to extract bioactive compounds along with the penetration capacity. These parameters depend on the solvent type and temperature (CEM 2022; Dąbrowska et al. 2018). Another important factor is the material of the reactor vessel. It should be composed of a material transparent to the microwave wavelength

Table 16.4 Values of ε' (dielectric constant), ε'' (dielectric loss factor), and tan δ (dissipation factor or loss tangent) for some solvents usually applied to extract bioactive compounds at 2.45 GHz, according to CEM (2022), Dąbrowska et al. (2018)

Solvent	ε'	ε''	tan δ	Penetration depth (cm)
Water	80.4	9.9	0.12	1.4 (45 °C)
Ethanol	24.3	22.87	0.94	–
Methanol	32.6	21.45	0.66	<1 (25 °C)
Acetone	20.7	1.12	0.05	7 (25 °C)

(or nonabsorbing material) that enables to avoid energy loss during crossing the reactor's walls (Dąbrowska et al. 2018).

In MAE, the effects of temperature and extraction time have to be joint evaluated on extraction. Both and its interaction affect the content of bioactive compounds (Gómez-Cruz et al. 2022). Temperature in the range of 60–90 °C is most frequently used in the case of MAE at atmospheric pressure, while using a closed vessel at higher temperatures can be tested (Kala et al. 2016). If temperature is not controlled, microwave power is an essential factor to be studied since it also affects temperature and thus the extraction efficiency (Xie et al. 2019). It has been suggested that at higher temperatures, the solvent viscosity is reduced, and the solubility of the target compounds favored thanks to the increasing intermolecular interaction and molecular motion. It also gives rise to an increased intracellular pressure, causing cell rupture and enhancing the transfer rate (da Rosa et al. 2019).

However, as for UAE, the application of high temperatures can degrade thermolabile bioactive compounds. Consequently, besides power and temperature, the effect of the extraction time should be evaluated. In fact, prolonged values of time, especially at high temperatures, can result in extreme overheating and the degradation and oxidation of the compounds of interest (da Rosa et al. 2019). In fact, short extraction times are required with MAE, which is one of its advantages of this technology (Ekezie et al. 2017). In MAE, depending on the biomass, conditioning, and extraction conditions, the temperature may vary at which the degradation of olive bioactive compounds occurs, including hydroxytyrosol and triterpenic acids; e.g., some authors have pointed out 50 and 80 °C when using OL and OP (Taamalli et al. 2012; Xie et al. 2019), while in other studies, the working temperature was 80 °C using OL (Cláudio et al. 2018). Also, other bioactive compounds could appear. For example, using steam explosion, the thermal degradation of oleuropein occurred at high temperatures (220 °C), but it produced an increase in hydroxytyrosol (Romero-García et al. 2016).

16.4.3 Supercritical CO_2 Extraction

A supercritical fluid has characteristics of both liquid and gas. The supercritical state is achieved when the substance is subjected to pressure and temperature above its

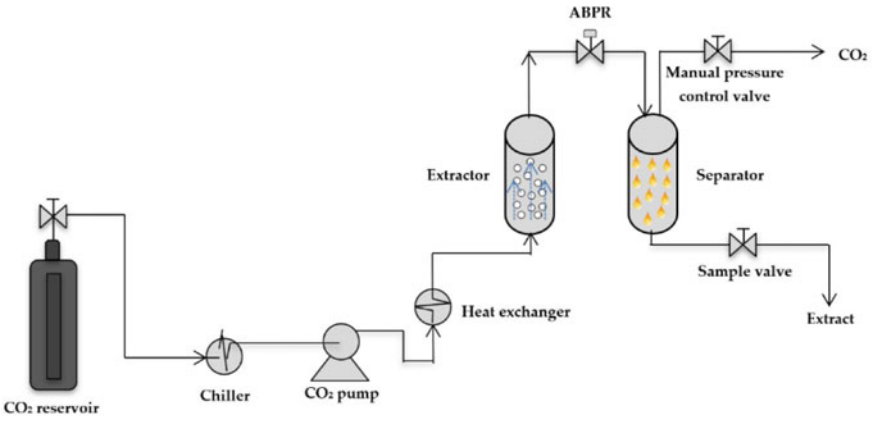


Fig. 16.7 Scheme of a supercritical CO_2 extractor, where ABPR is the automatic back pressure regulator (Cerón-Martínez et al. 2021)

critical point (Yahya et al. 2018). In this type of extraction, two stages take place: the solubilization of the bioactive compounds present in the biomass and their separation from the supercritical solvent by reducing pressure and/or increasing temperature (Fig. 16.7) (da Silva et al. 2016).

For the extraction of bioactive compounds, the physicochemical properties, including density and polarity, of the supercritical fluid can be modified by controlling pressure, temperature, and cosolvent %, which is generally ethanol (Hall et al. 2018; Difonzo et al. 2021; Katsinas et al. 2021). The flow rate of CO_2 and the extraction time can also be optimized to maximize yields. High solvent flow rate increases the number of CO_2 molecules in contact with the bioactive compound (Hall et al. 2018).

The application of high temperature increases the extraction of hydroxytyrosol, while it decreases oleuropein due to its conversion into the former by hydrolysis. This parameter, cosolvent, and their joint effect are going to modulate the polarity as well as the compounds extracted (Katsinas et al. 2021). These authors proposed the application of 66 °C and 10% ethanol to obtain an extract rich in oleacein (52 mg/g dry extract), while the extraction at 184 °C and 90% ethanol favored the extraction of the polar compound hydroxytyrosol (9.5 mg/g dry extract) from defatted OP. For mannitol extraction from OL, it has been shown that 200–350 bar increases the extraction yield, while a low temperature and the use of 17% ethanol also favor the extraction (Ghoreishi et al. 2009). Triterpenic acids can be extracted with higher yields than phenolic compounds using dry OL and applying 150 bar, 40 °C, and 6.6% ethanol (Taamalli et al. 2020). Alternatively, using CO_2 without adding a cosolvent can be applied to reduce the polarity and recover squalene and tocopherols (Difonzo et al. 2021).

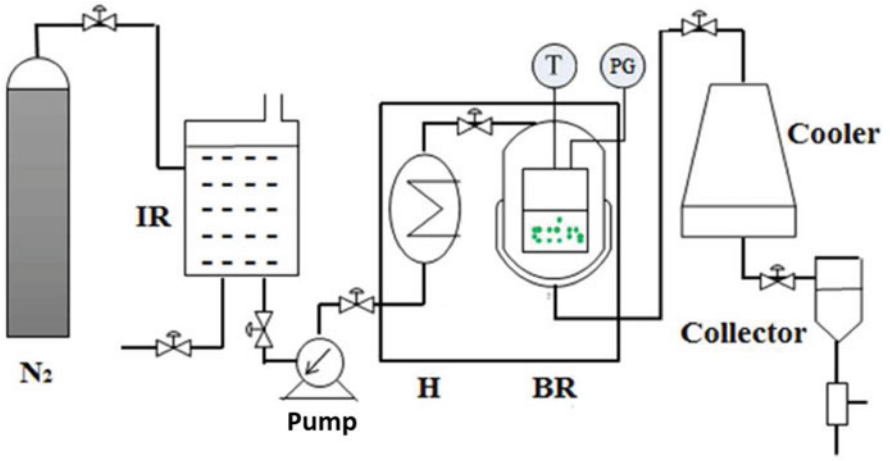


Fig. 16.8 Scheme of a pressurized liquid extractor, where BR, IR, PG, H, and T are the batch reactor, impounding reservoir, pressure gauge, preheater, and thermocouple, respectively (Xiao et al. 2017)

16.4.4 Pressurized Liquid Extraction

PLE is also known as accelerated solvent extraction and pressurized solvent extraction. It is based in the application of relatively high pressure (35–200 bar) and temperature (25–200 °C) with 5–15 min extraction time for one or various extraction cycles (Tsiaka et al. 2017). Figure 16.8 shows a scheme of a PLE device.

When the extraction agent is water, subcritical conditions can be applied and then the extraction can be called subcritical water extraction (SWE). For this purpose, higher pressures than 10 bar have to be applied to maintain the liquid state of water using the temperature domain between 100 °C (boiling point) and 374 °C (critical temperature) (Contreras et al. 2019). SWE provides short extraction times and low solvent consumption, but the main disadvantage is the degradation of bioactive compounds when applying high temperatures for extraction (Essien et al. 2020). Therefore, time and temperature should be optimized together. Lama-Muñoz et al. (2019b) have shown that the content of oleuropein and luteolin-7-*O*-glucoside from OL are maximized at 5% moisture and using 190 °C for 5 min with 80% v/v ethanol as solvent and one extraction cycle. These authors also showed that mannitol can be coextracted using these conditions (Lama-Muñoz et al. 2020). However, the highest yield of mannitol from OL was obtained at about 100 °C and 5 MPa. Then, for higher temperatures and pressure, the yield decreased (Ghoreishi and Shahrestani 2009b).

The increase in temperature and pressure can allow an improvement in the extraction of the compounds of interest related to a greater penetration of the solvent in the biomass matrix (Li et al. 2019). However, besides potential degradation, another aspect that should be considered is that, at high temperatures, undesirable compounds for human consumption can be generated, such as furfural and

hydroxymethylfurfural (Vladić et al. 2020). It has been suggested that a high increase in these sugar derivatives occurs when the temperature rises from 160 °C (Kanmaz 2018).

16.4.5 Electro-Based Extraction

The use of electro-based technologies enhances extraction and diffusion of compounds using nonthermal conditions (Contreras et al. 2019). Among these technologies, pulsed electric field (PEF) and high-voltage electric discharge (HVED) have been applied for the recovery of bioactive compounds from olive-derived biomasses. In PEF an electrical potential is applied. In HVED direct energy is released into the medium through a plasma channel formed by a HVED between two electrodes submerged into the solvent. Both technologies disrupt biomass tissues, increase the migration of intracellular water and solutes, accelerate the mass transfer, and enhance the extraction of bioactive compounds (Roselló-Soto et al. 2015; Pappas et al. 2021). It has been suggested that electroporation phenomenon takes place in PEF in a nondestructive way, i.e., the formation of pores is electrically induced in the lipid bilayer of membranes under the influence of an induced transmembrane voltage (Pappas et al. 2021). A PEF system is shown in Fig. 16.9. In addition, Fig. 16.10 shows the scheme of a HVED equipment.

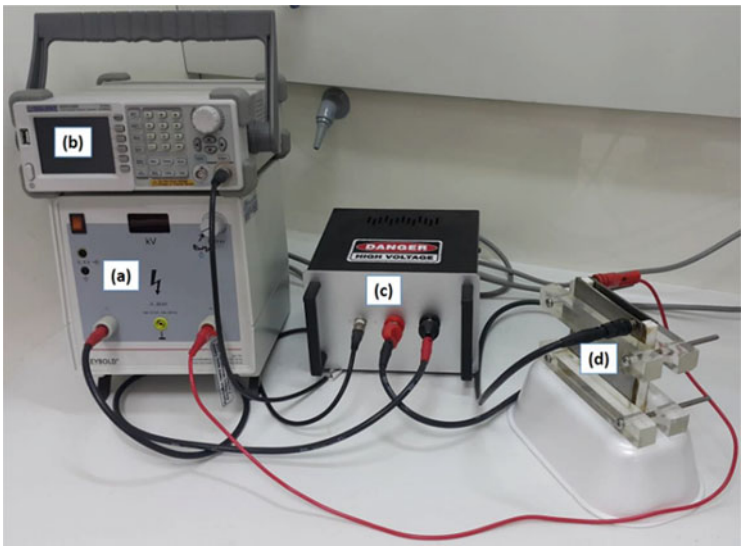


Fig. 16.9 Pulsed electric field system, consisting of (**a**) high-voltage power generator, (**b**) function/arbitrary waveform generator, (**c**) electronic switch circuit, and (**d**) treatment chamber (Pappas et al. 2021)

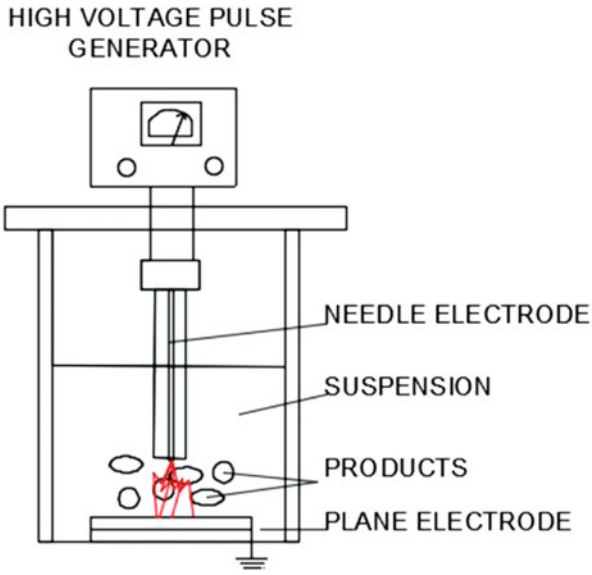


Fig. 16.10 Scheme of a high-voltage electric discharge extractor (Lampakis et al. 2021)

Specific PEF operating factors are electric field strength, pulse shape and duration, and specific energy, which could be optimized to maximize the content of bioactive compounds (Pappas et al. 2021). Similarly, HVED-based extraction is affected by the latter parameters (Roselló-Soto et al. 2015). Pappas et al. (2021) showed that the PEF conditions, e.g., the pulse duration between 10 and 100 μs, can also be modulated to selectively extract bioactive compounds. For example, a large number of short-duration pulses led to higher recovery of total phenolic compounds from OL, while the extraction of oleuropein, with a more apolar feature, was increased under a 100-μs pulse.

16.4.6 Examples of Application

Table 16.5 provides some examples of the application of green technologies to extract phenolic compounds from olive-derived biomasses. Comparing these biomasses, OL, OML, OP, and EOP are the best ones to solubilize phenolic compounds. UAE, MAE, PLE, and PEF have been applied for this purpose using water, alcoholic water solutions, or acetonic water solutions, mainly. The results were similar to those obtained by conventional technologies. Among these solvents, water is a desirable extractive agent to be applied since it is cheap and not toxic, while the other solvents are also applied in the food industry. The application of water as extractive agent of OL resulted in more solubilization of hydroxytyrosol when using MAE at 80 °C, but the use of ethanolic-water solutions led to increased oleuropein content (Sánchez-Gutiérrez et al. 2021). Interestingly, hydroxytyrosol can be efficiently extracted from

Table 16.5 Extraction of phenolic compounds from olive-derived biomasses by several technologies and conditions

Biomass	Conditioning	Extraction technology	Extraction solvent and conditions	Main bioactive compounds	References
Olive tree pruning	Drying, milling 4 mm	Maceration	50% ethanol	TPC: 23.9 mg/g[a]	Gullón et al. (2018)
			17% w/v, 90 min, 55 °C		
	Drying, milling 1 mm	Probe-type ultrasound	55% ethanol	TPC: 31.0 mg/g[a]	Martínez-Patiño et al. (2019)
			5% w/v, 15 min, 70% amplitude, 400 W, 24 kHz		
	Drying, milling, sieving 40 mesh	Soxhlet	Water	TPC: 35.3 mg/g[a]	Doménech et al. (2021)
			2% w/v, overnight	Hydroxytyrosol: 1.9 mg/g[a]	
Olive leaves	Drying, milling 1.2 mm	Probe-type ultrasound	60% ethanol	TPC: 35.8 mg/g[a]	Lama-Muñoz et al. (2019b)
			7.7% w/v, 40 °C, ≈15 min, 30% amplitude, 150 W, 40 kHz	Oleuropein: 69.9 mg/g[a]	
				Luteolin-7-*O*-glucoside: 1.8 mg/g[a]	
	Drying, milling 1.2 mm	Pressurized liquid	60% ethanol	TPC: 45.9–59.3 mg/g[a,b]	Lama-Muñoz et al. (2019a)
			14% w/v, 190 °C, 5 min	Oleuropein: 43.4–115.0 mg/g[a,b]	
				Luteolin-7-*O*-glucóside: 0.9–3.8 mg/g[a,b]	
	Drying, milling 1.2 mm	Soxhlet	60% ethanol	TPC: 42.5–60.2 mg/g[a,b]	Lama-Muñoz et al. (2019a)
			4 h	Oleuropein: 49.1–122.3 mg/g[a,b]	
				Luteolin-7-*O*-glucoside: 1.3–4.7 mg/g[a,b]	
		Steam explosion	180 °C, 8.3 min	TPC: 44.8 mg/g[a]	Romero-García et al. (2016)
				Oleuropein: 15.8 mg/g[a]	
				Hydroxytyrosol: 3.4 mg/g[a]	

	Drying, milling	Bath-type ultrasound	80% ethanol	TPC: 56.2 mg/g[a]	Giacometti et al. (2018)
			6.7% w/v, 60 °C, ≈4 min, 70% amplitude	Oleuropein: 13.4 mg/g[a]	
				Luteolin-7-*O*-glucoside: 0.5 mg/g[a]	
	Drying, milling 1 mm	Bath-type ultrasound	6% w/v, 47% ethanol, 50 min, 40 kHz	TPC: 27.5–49.2 mg/g[a,b]	Medfai et al. (2020)
	Drying, milling 1 mm	Maceration	10% w/v, 80% ethanol, 24 h, room temperature, 150 rpm	TPC: 33.9–54.9 mg/g[a,b]	Medfai et al. (2020)
	Drying, milling 0.8 mm	Pulsed electric field	50% v/v ethanol, 10-μs pulse duration, 30 min, 1 kV/cm	TPC: 30.5 mg/g[a]	Pappas et al. (2021)
				Luteolin-7-*O*-glucoside, apigenin-7-*O*-rutinoside	
	Drying	Microwave-assisted extraction (closed vessels)	Choline chloride-ethylene glycol (1:2) with 43.3% water	Oleuropein: 10.6 mg/g[a]	Alañón et al. (2020)
			79.6 °C, 16.7 min		
	Drying, milling <0.3 mm	High-electric-voltage discharge	2% w/v, 50% ethanol, argon at 20 kV for 9 min	TPC: 66.0 mg/g[a]	Žuntar et al. (2019)
	Drying, milling <2 mm	Microwave-assisted extraction (closed vessels)	50% ethanol	Oleuropein: 40.6 mg/g	Sánchez-Gutiérrez et al. (2021)
			80 °C, 10 min		
	Drying, milling	Supercritical fluid	CO_2, 6.6% ethanol	Oleuropein: 0.0005–2.9 mg/g[c]	Taamalli et al. (2020)
			150 bar, 40 °C, 1 h, 23 g/min		
Olive mill leaves	Drying, milling 4 mm	Maceration	50% ethanol	TPC: 27.5 mg/g[a]	Gullón et al. (2018)
			17% w/v, 90 min, 55 °C		
	Drying, milling 1 mm	Probe-type ultrasound	51% ethanol	TPC: 42.0 mg/g[a]	Martínez-Patiño et al. (2019)
			5% w/v, 15 min, 70% amplitude, 400 W, 24 kHz		
	Drying, milling, sieving 40 mesh	Soxhlet	Water	TPC: 43.7 mg/g[a]	Doménech et al. (2021)
			2% w/v, overnight	Hydroxytyrosol: 1.0 mg/g[a]	

(continued)

Table 16.5 (continued)

Biomass	Conditioning	Extraction technology	Extraction solvent and conditions	Main bioactive compounds	References
	Drying and milling (1 mm)	Bath-type ultrasound	47% ethanol	TPC: 20.6 mg/g[a]	Contreras et al. (2020a, b)
			6% w/v, 5 min, 40 kHz	Oleuropein: 5 mg/g[a]	
Olive pomace	Drying and milling (0.35 mm)	Probe-type ultrasound	90% ethanol	Hydroxytyrosol: 55.10 mg/g[d]	Xie et al. (2019)
			3.3 w/v, 50 °C, 5 min, 135.6 W/cm^2, 20 kHz		
	Drying and milling (0.35 mm)	Microwave, 2450 MHz	90% ethanol	Hydroxytyrosol: 53.20 mg/g[d]	Xie et al. (2019)
			3.3 w/v, 50 °C, 600 W, 3 min		
Exhausted olive pomace	Drying and milling (1 mm)	Bath-type ultrasound	47% ethanol	TPC: 44.5 mg/g[a]	Contreras et al. (2020a)
			6% w/v, 5 min, 40 kHz	Hydroxytyrosol: 8.0 mg/g[a]	
	Drying, milling, sieving 40 mesh	Soxhlet	Water	TPC: 65.6 mg/g[a]	Doménech et al. (2021)
			2% w/v, overnight	Hydroxytyrosol: 4.1 mg/g[a]	
				Tyrosol: 0.8 mg/g[a]	
Olive pits	Drying, milling, sieving 40 mesh	Soxhlet	Water	TPC: 6.1 mg/g[a]	Doménech et al. (2021)
			2% w/v, overnight	Hydroxytyrosol: 0.1 mg/g[a]	
				Tyrosol: 0.4 mg/g[a]	
	Cleaning and drying	Autoclave	Water	TPC: 3.9 mg/g[a]	Lama-Muñoz et al. (2014)
			50% w/w, 130 °C, 90 min	3,4-dimethoxybenzoic acid	
	Agitation 20 min	High-electric-voltage discharge	10% w/w, 49% ethanol, pH 2.5	TPC: 106.4–618.9 mg/L[b]	Roselló-Soto et al. (2015)
			66 kJ/kg, 20 °C, 10-μs pulse duration, 4 ms		
Residual pulp	Drying and milling (1 mm)	Bath-type ultrasound	47% ethanol	TPC: 4.6 mg/g[a]	Contreras et al. (2020a)
			6% w/v, 5 min, 40 kHz		

The total phenolic content (TPC) is expressed as gallic acid equivalents

[a] Referred to dry biomass weight

[b] Depending on the cultivar

[c] Depending on the drying method and sampling time

[d] The basis is not defined

EOP using water aided by ultrasound (Gómez-Cruz et al. 2021b). CO_2 is also generally recognized as safe (GRAS) by the Food and Drug Administration and the European Food Safety Authority, but its uses are limited to SCE (Difonzo et al. 2021). Another current trend is the application of deep eutectic solvents (DESs) to substitute organic solvents, especially those from natural origin (NADESs) and with low toxicity. NADESs are a mixture of two or more components, where one acts as hydrogen bond acceptor (HBA) and the other as hydrogen bond donor (HBD), in solid or liquid state. This mixture is formed at a particular molar ratio to become liquid at room temperature (Alañón et al. 2020). Some studies have combined NADES with MAE and the results were satisfactory in terms of extraction of oleuropein from OL and olive fruits (Alañón et al. 2020; Bonacci et al. 2020). Nonetheless, alcoholic solutions seem to solubilize the major content of this compound when using OL (Table 16.5). Therefore, the solvent choice will depend on the yield, desired bioactive compound type to be extracted, and technology.

Also, note that NADESs should present the desirable characteristics for extraction solvents in MAE, which were showed in Sect. 16.4.2. NADESs are viscous solutions, and in the case of ultrasound, water can be added to reduce the viscosity of the NADES solution and favor cavitation (Patil et al. 2021) and the contact of the biomass with the solvent (Liang et al. 2020). Twenty percent water can be enough to reduce viscosity and at the same time to maintain the hydrogen-bonding properties (Chanioti and Tzia 2018; Bonacci et al. 2020). Nonetheless, 20% water-NADES based on choline chloride as HBA has showed better results to extract phenolic compounds from OP using simply homogenization compared to UAE and MAE (Chanioti and Tzia 2018). Future studies can address promising results combining NADES and these technologies.

The application of these technologies to recover mannitol and triterpenic acids has a lower number of examples (Table 16.6). OL, OML, OP, EOP, and residual pulp are rich sources of these components. However, in the case of triterpenic acids, OL and OML may contain maslinic, oleanolic, ursolic, and pomolic acids, while maslinic and oleanolic acids have been detected in OP, EOP, and residual pulp (Romero et al. 2017; Taamalli et al. 2019; Contreras et al. 2021).

Most studies on mannitol have been performed using water as solvent and the studies suggest that the yield of mannitol is in the same order of magnitude than conventional extraction (Table 16.6). Ghoreishi and Shahrestani (2009a) suggested that the distribution coefficient, defined as volume of fluid phase/mass of biomass, for SWE was lower than that for SCE and Soxhlet extraction, which meant that a lower solvent amount is required per gram of biomass to extract mannitol. SWE also offered the highest yield. In this case, the use of water as solvent can explain in part the highest yield since mannitol presents high solubility in water (Table 16.2). Nonetheless, as commented before, mannitol can be coextracted with phenolic compounds (Kashaninejad et al. 2020; Contreras et al. 2021). Therefore, for further separation, a purification technology will be required.

Regarding triterpenic acids, most studies applied pure or nearly pure organic solvents. Since these triterpenes are slightly polar compounds, medium-polar solvents can be applied, such as ethanol, methanol, *n*-butanol, ethyl ether, etc. (Castellano et al. 2022). Alternatively, Taamalli et al. (2019) applied supercritical

Table 16.6 Extraction of mannitol and triterpenic acids from olive-derived biomasses by several technologies and conditions

Biomass	Conditioning	Extraction technology	Extraction solvent and conditions	Content	References
Mannitol					
Olive tree pruning	Drying, milling, sieving 40 mesh	Soxhlet	Water	32.9 mg/g[a]	Doménech et al. (2021)
			2% w/v, overnight		
Olive leaves	Drying, milling 1.2 mm	Pressurized liquids	60% ethanol	29.7–63.7 mg/g[a]	Lama-Muñoz et al. (2020)
			14% w/v, 190 °C, 5 min		
	Drying, milling 1.2 mm	Soxhlet	60% ethanol	31.7–82.2 mg/g[a]	Lama-Muñoz et al. (2020)
			4 h		
		Steam explosion	180 °C, 8.3 min	52.0 mg/g[a]	Romero-García et al. (2016)
	Sieving with mesh size of 18–35, drying	Pressurized liquid	Water	76.75% w/w[b]	Ghoreishi and Shahrestani (2009b)
			100 °C, 5 MPa, 5 min		
	Drying, sieving with mesh size of 18–35	Supercritical fluid	CO_2, 20% ethanol	1.1% w/w[b]	Ghoreishi et al. (2009)
			350 bar, 40 °C, 90 min		
	Drying, sieving with mesh size of 18–35	Soxhlet	Ethanol	57.3% w/w[b]	Ghoreishi et al. (2009)
			8 h		
Olive mill leaves	Drying, milling, sieving 40 mesh	Soxhlet	Water	9.6 mg/g[a]	Doménech et al. (2021)
			2% w/v, 12 h		
	Drying, milling 1 cm	Autoclave	Water	35.9 mg/g[a]	López-Linares et al. (2019)
			5% w/v, 100 °C, 90 min		
EOP	Drying, milling, sieving 40 mesh	Soxhlet	Water	36 mg/g[a]	Doménech et al. (2021)
			100 °C, 5 MPa, 5 min		
Olive pits	Drying, milling, sieving 40 mesh	Soxhlet	2% w/v, overnight	0.2 mg/g[a]	Doménech et al. (2021)

Triterpenic acids					
Olive leaves	Drying, homogenization/ crushing	Bath-type ultrasound-assisted extraction	100% ethanol	Oleanolic acid: 18.9–39.8 mg/g[a,c]	Martín-García et al. (2019)
			2% w/v, 60 °C, 30 min	Maslinic acid: 1.9–5.9 mg/g[a,c]	
				Ursolic acid: 1.8–4.9 mg/g[a,c]	
	Milling, freeze-drying	Reflux	Dichloromethane/methanol (2:1)	Oleanolic acid: 0.07 mg/g[a]	Stiti and Hartmann (2012)
			65 °C, 2 h	Maslinic acid: 2.8 mg/g[a]	
	Drying	Maceration	Ethanol	Oleanolic acid: 29.2–34.5 mg/g[a,c]	Guinda et al. (2010)
			5% w/v, 25 °C, 1 h with occasional shaking	Maslinic acid: 4.8–7.3 mg/g[a,c]	
				Ursolic acid: 2.0–2.5 mg/g[a,c]	
	Drying, milling	Supercritical fluid	CO_2, 6.6% ethanol	Oleanolic acid: up to ~11 mg/g[a,c]	Taamalli et al. (2019)
			150 bar, 40 °C, 1 h, 23 g/min	Maslinic acid: up to ~2 mg/g[a,c]	
				Ursolic acid: up to ~17 mg/g[a,c]	
Olive pomace	Drying and milling (0.35 mm)	Probe-type ultrasound	90% ethanol	Oleanolic acid: 30.8 mg/g[d]	Xie et al. (2019)
			3.3 w/v, 50 °C, 5 min, 135.6 W/cm^2, 20 kHz	Maslinic acid: 381.2 mg/g[d]	
	Drying and milling (0.35 mm)	Microwave, 2450 MHz	90% ethanol	Oleanolic acid: 26.3 mg/g[d]	Xie et al. (2019)
			3.3 w/v, 50 °C, 600 W, 3 min	Maslinic acid: 356.3 mg/g[d]	

(continued)

Table 16.6 (continued)

Biomass	Conditioning	Extraction technology	Extraction solvent and conditions	Content	References
Exhausted olive pomace	Probe-type ultrasound	Maceration	Ethanol	Oleanolic acid: 0.3 mg/g[e]	Gómez-Cruz et al. (2021b)
			Room temperature, 24 h, 150 rpm	Maslinic acid: 8.4 mg/g[e]	
Residual pulp	Milling	Agitation	Methanol/ethanol (1:1)	Maslinic acid: up to 84 mg/g[a,f]	Romero et al. (2017)
			2.5% w/v, 1 min		

[a] Referred to dry biomass weight
[b] Recovery
[c] Depending on the cultivar and/or sampling time
[d] The basis is not defined
[e] Extracted solid
[f] Depending on the olive oil mill where the sample was collected

CO_2 with a small percent of ethanol (7%, approximately). The addition of aqueous or ethanol as cosolvent can improve the extraction efficiency of triterpenic acids by modifying the polarity of the supercritical CO_2 (Castellano et al. 2022). As commented before, these compounds present more apolar characteristics and poor solubility in water (Table 16.2). This has been the basis of a recent work on EOP to sequentially extract hydroxytyrosol and mannitol with water by probe-type ultrasound and then triterpenic acids using ethanol (Gómez-Cruz et al. 2021b). This study suggested that the application of a first extraction step favored the extraction of triterpenic acids from this biomass.

16.5 Large-Scale Extraction

The potential application of bioactive compounds in different sectors brings the necessity to determine the most efficient and sustainable extraction technology and conditions. In general, the large-scale extraction of bioactive compounds has low Technology Readiness Level, especially when considering olive bioactive compounds. Most of the aforementioned studies were performed at lab scale, but studies on large application of some technologies have been performed with other agri-food biomasses. Among the green extraction technologies, UAE is considered a rapid and cost-efficient extraction method, with potential application in the extraction of natural compounds. Some devices are already available in the market to perform extractions at a large scale; for example, the company SARL REUS has developed bath-type ultrasonic reactors with a capacity of 30–1000 L. Hielscher Ultrasound Technology employs discontinuous and continuous equipment based on the probe system (Mason et al. 2015). Some changes may occur in the results when moving from lab to pilot scale caused by different energy inputs of the equipment (Contreras et al. 2019). However, better results can be obtained compared to conventional maceration when using batch conditions (30-L reactor), while multistage cross-current extraction does not offer higher improvements because extraction is more effective during the first minutes and then it decreases (Meullemiestre et al. 2016). Multiple transducer flow reactors operating at high power density have shown adequate process intensification (Alexandru et al. 2013). The MAE design to recover natural compounds at large scale will depend on the sample thickness and the frequency of the microwaves to enable the penetration of the electromagnetic waves. Nonetheless, the scaling up of 915-MHz continuous flow process could be an option (Radoiu et al. 2019). Although this technology is still in its infancy (Ciriminna et al. 2016), there are continuous industrial-scale extractors using microwave radiation (SAIREM 2021). Large-scale applications of SCE have also been performed using tubular extractor of 3 L to recover olive bioactives (Katsinas et al. 2021). There is available technology at the industry for the extraction of natural compounds and hop constituents and decaffeination of tea and coffee (Knez et al. 2019), and so the industrial deployment is feasible. Concerning electrotechnologies, pilot-scale experiments (35 L) on grape pomace with HVED have shown that higher treatment energies are required to obtain similar yields than at lab scale (1 L).

Moreover, the specific energy input per pulse was in both cases 0.53 kJ/kg to produce shock waves of similar pressure values (≥100 bar) for the extraction of phenolic compounds (Boussetta et al. 2012). SWE had also promising results to extract flavonoids at pilot scale (8 L). Nonetheless, few industrial applications exist probably due to the range of operating temperatures and pressures and the mode of operation of SWE (Essien et al. 2020).

Comparing the technologies, it seems that the capital costs of MAE and SCE is medium and higher, respectively, compared to UAE, while the operating costs of MAE and UAE are medium and the SFE low. It has been estimated that the total value for UAE, MAE, and SCE could be around 86–157, 114–143, and 143–238 €/kg extract, respectively (Talmaciu et al. 2015). In this sense, higher capital costs imply longer payback periods (Essien et al. 2020). Nonetheless, it will also depend on the extraction conditions and the size of the plant (Tsiaka et al. 2017). Concerning the extraction conditions, modeling of the extraction processes at laboratory scale can provide a better understanding of the operational parameters and mechanisms to scale up the optimized conditions (Tsiaka et al. 2017; Gómez-Cruz et al. 2021b). However, when moving to the industrial scale, the economy can govern the values of some operational parameters. For example, the application of high solvent ratios to biomass, which are usually applied in lab studies, will require larger and more expensive equipment (Croxatto-Vega et al. 2021), but high solid loadings will reduce the internal mass transfer (Katsinas et al. 2021). So a compromise between the obtainment of the yield of bioactive compounds, richness, and solid loading has to be found (Contreras et al. 2020b). In this context, techno-economic analysis and scaling at least using computer-aided tools can shed light into the economy of the extraction process. Croxatto-Vega et al. (2021) found that PLE operating at a solvent ratio to biomass of 50 kg/kg, which had the higher extraction yield of phenolic compounds from wine pomace, did not compensate the higher costs compared to the operation with ratios (25 and 10 kg/kg). Concerning olive-derived biomasses, very few studies dealt with the economic viability and some theoretical techno-economic studies have been performed using conventional technologies for extraction on OML (Solarte-Toro et al. 2018) and OTP (Solarte-Toro et al. 2019). These studies integrated the extraction step, with solid loadings ~15% w/v, in a biorefinery scheme to also obtain bioethanol. The overall costs were influenced by the prices of the biomass (Solarte-Toro et al. 2018). The cost of the biomass introduces some uncertainty to the economic profit. While OTP, which is generated in the field, will incur cost associated with collection and transport, OML, OP, OS, and residual pulp are accessible at the industry, favoring their conversion (Galán-Martín et al. 2022). Today, OML and OP have no (or very little) benefit for the oil mill, while OS and EOP have established markets and so relatively higher prices (Galán-Martín et al. 2022).

The economy of the large-scale development of the extraction process is also going to be affected by the following:

- The conditioning (drying, milling, etc.) prior to the extraction of bioactive compounds. Drying enables the storage of the biomass for a longer period of time, standardizes the moisture, and limits the microbial spoilage and enzymatic

degradation. Also, it can favor the extraction time of phenolic compounds depending on the extraction conditions and the type of drying (Lama-Muñoz et al. 2019a; Difonzo et al. 2021). Milling increases mass transfer and most studies applied a milling step (Tables 16.5 and 16.6). Nonetheless, Gómez-Cruz et al. (2020) and Gómez-Cruz et al. (2021b) have found that the industrial EOP can be directly applied for extraction when using high-potency probe-type UAE and hydrothermal extraction at high temperatures. This means a save in the overall processing costs.

- The separation technology and performance after extraction. Decantation, filtration, or centrifugation can be applied to separate the solvent from the extracted biomass. The solvent retention capacity of the biomass will also determine the real recovery of the compounds and it depends on the biomass type (Contreras et al. 2021).
- Depending on the application, it could be desirable to obtain extracts with higher purity to that obtained by purely extraction. The purity obtained during the extraction step is limited due to the co-extraction of other extractable compounds. There are several approaches that can be performed to achieve purities from over 20% to 40%, such as membrane filtration, adsorption, and liquid-liquid extraction, which can be applied solely or in combination. To produce highly pure compounds (>90%), a chromatographic separation can be applied (Britton et al. 2019) (Fig. 16.11).
- Drying the extract can convert the liquid extracts into storable commodities since it can improve the stability compared to that of liquid extracts, while the transport and storage become easier. For this purpose, oven-drying, freeze-drying, and spray-drying have been applied (Kiritsakis et al. 2018; Gómez-Cruz et al. 2021a). The quality of the product, the application, and the economy of the process will address the choice of the drying technology.

Once the cost of the whole process is estimated, the price of the marketed extracts will influence the economic viability and provide uncertainty (Tsiaka et al. 2017; Orive et al. 2021). Therefore, the deployment of these green technologies will go hand in hand with market studies of the expected marketed product. If these processes are more respectful with the environment, it can be a claim for consumers and to obtain certifications, e.g., the EU ecolabel, which recognizes goods and services with high environmental standards through their whole life cycle (European Commission 2022).

In this sense, for the successful implementation of the green extraction process, not only economic but also sustainability aspects should be considered in the transition towards a more sustainable food system. However, most of the studies do not provide the energy requirement of the overall extraction process. Comparing some of the technologies, Roselló-Soto et al. (2015) evaluated UAE, HVDE, and PEF treatments on olive kernel extraction, varying the extraction energy inputs from 18 to 109 kJ/kg. Their results showed that the technology and energy input showed differences on the extraction of phenolic compounds, being a more efficient HVED. On the basis of 1 kWh equals 800 g CO_2, Xie et al. (2019) highlighted that UAE can be advantageous in terms of energy efficiency and carbon emission compared to

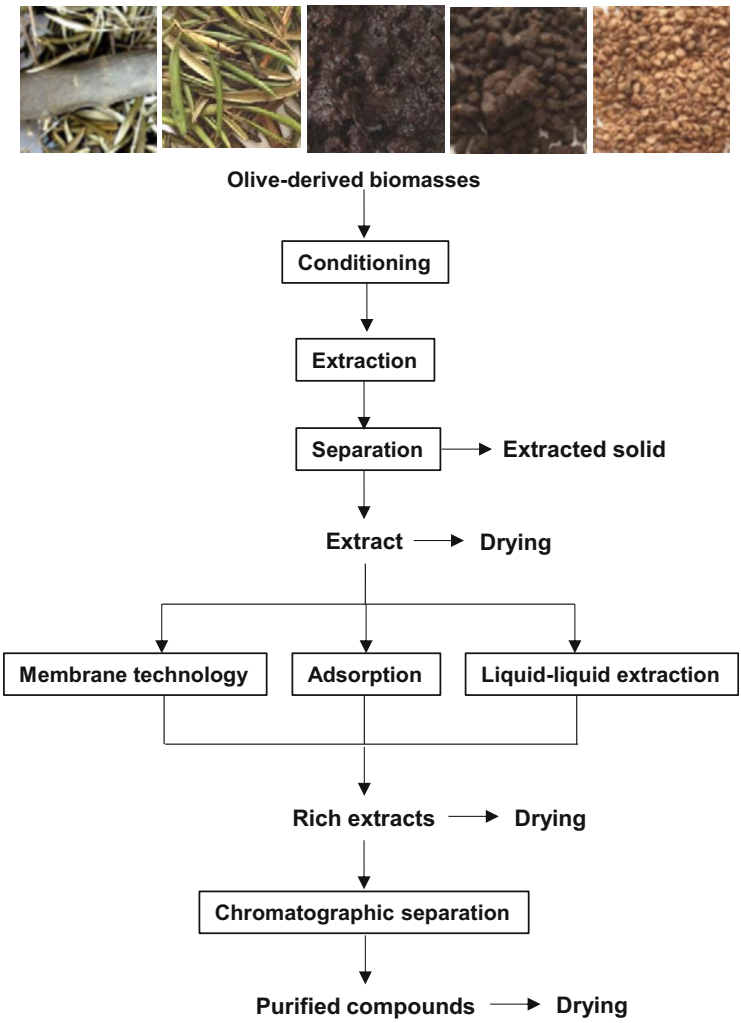


Fig. 16.11 Summarized scheme of the overall process to obtain rich extracts and purified compounds from olive-derived biomasses. (Based on Britton et al. 2019)

MAE and conventional extraction. Another important aspect to bear in mind for the selection of the extraction process is to perform a life cycle assessment (LCA), which can shed light on the overall environmental impact, including the carbon footprint (Croxatto-Vega et al. 2021). The use of an organic solvent like ethanol introduces a higher environmental impact per amount of phenolic compound than using water although a green technology is applied. Moreover, the heat recovery in an upscaled process is crucial to reduce 35–60% net heat demand (Carlqvist et al. 2022), as well the recycling of the solvent (Essien et al. 2020). It would be also interesting to compare conventional solvents and NADESs for the extraction of olive-derived

bioactives using techno-economic assessment and LCA. NADESs are biodegradable and present low toxicity, but their cost can be higher than water or common solvents. For example, choline chloride, which is a common HBA, costs about 150 €/kg (Bonacci et al. 2020). Therefore, all these aspects have to be considered in future studies to provide sustainable extraction processes. Also, the profitability of the combination of two extraction technologies, such as MAE with ultrasound, subcritical and supercritical fluids, to boost extraction efficiency deserves further study (Ekezie et al. 2017).

16.6 Conclusions

There is a great scientific interest in the application of green technologies to extract bioactive compounds from olive-derived biomasses, and numerous studies are available in literature. Nonetheless, the technology has to be competitive with conventional extraction not only in terms of extraction efficiency but also regarding economy and sustainability aspects. More advance studies should be done combining all these aspects and to find market niches for these extracts. Moreover, other aspects, which were not the objective of this review, such as quality and toxicity of the extracts, should be considered (Fig. 16.12). The integration of the extraction

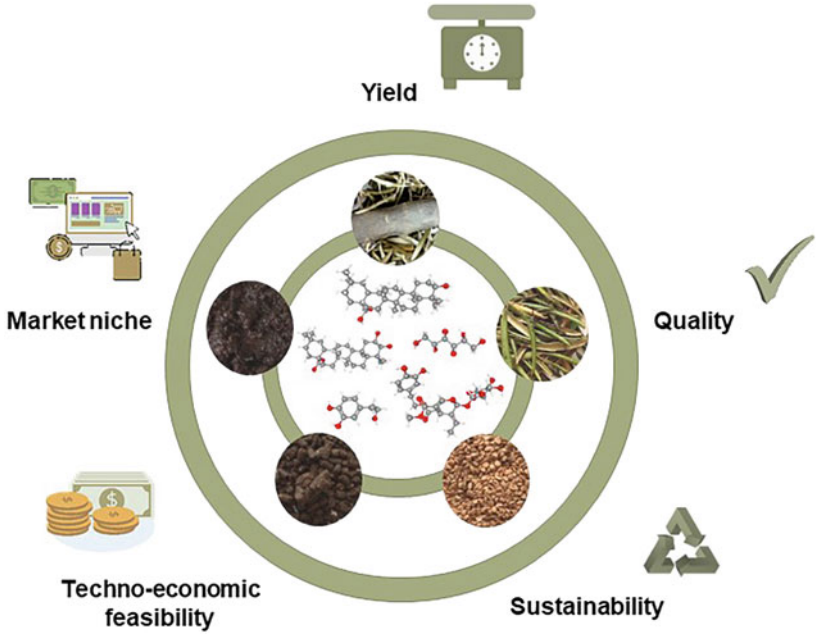


Fig. 16.12 Some aspects to be considered for further development of green technologies in the extraction field of bioactive compounds from olive-derived biomasses

under biorefinery schemes is also other target to move towards circular bioeconomy models.

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Chapter 17
Production and Use of Hydrolates from the Distillation Process of Aromatic Plants

Milica G. Aćimović

Abstract Lavender (*Lavandula* sp.), thyme (*Thymus* sp. and *Thymbra* sp.), oregano (*Origanum* sp.), savory (*Satureja* sp.), mints (*Mentha* sp.), sage (*Salvia officinalis* and *S. sclarea*), rosemary (*Rosmarinus officinalis*), rose (*Rosa* sp.), citrus (*Citrus* sp.), and bay laurel (*Laurus nobilis*) are species widely used as medicinal and aromatic plants. Their essential oils are a well-known resource of biological activities, applicable in food, cosmetic, and pharmaceutical industries, as well as in agriculture. Due to developments in ecology and sustainability during the past two decades, hydrolates, which were considered waste material for a long time, are viewed as by-products with promising activity and applications. This chapter provides a review of these ten hydrolates, their chemical composition, and potential use.

Keywords Essential oils · By-products · Hydrolate · Hydrosol · Food · Cosmetic · Pharmaceuticals

Abbreviations

$\bullet O_2^-$	superoxide anion radical
•OH	hydroxyl radical
A. bohemicus	*Acinetobacter bohemicus*
A. butzleri	*Arcobacter butzleri*
A. citri	*Alternaria citri*
A. cryaerophilus	*Arcobacter cryaerophilus*
A. fumigatus	*Aspergillus fumigatus*
A. hydrophila	*Aeromonas hydrophila*
A. lanthieri	*Arcobacter lanthieri*
A. mali	*Alternaria mali*
A. nidulans	*Aspergillus nidulans*

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A. niger	*Aspergillus niger*
A. oryza	*Aspergillus oryza*
A. parasiticus	*Aspergillus parasiticus*
A. skirrowii	*Arcobacter skirrowii*
A. sydowii	*Aspergillus sydowii*
A. thereius	*Arcobacter thereius*
A. vitis	*Allorhizobium vitis*
ABTS	2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)
B. amyloliquefaciens	*Bacillus amyloliquefaciens*
B. brevis	*Bacillus brevis*
B. cereus	*Bacillus cereus*
B. cinerea	*Botrytis cinerea*
B. subtilis	*Bacillus subtilis*
C. acnes	*Cutibacterium acnes*
C. albicans	*Candida albicans*
C. circinans	*Colletotrichum circinans*
C. herbarum	*Cladosporium herbarum*
C. sphaerospermum	*Cladosporium sphaerospermum*
C. violaceum	*Chromobacterium violaceum*
DPPH	2,2-diphenyl-1-picrylhydrazyl
E. aerogenes	*Enterobacter aerogenes*
E. amylovora	*Erwinia amylovora*
E. carotovora	*Erwinia carotovora*
E. coli	*Escherichia coli*
E. faecalis	*Enterococcus faecalis*
E. faecium	*Enterococcus faecium*
F. oxysporum	*Fusarium oxysporum*
F. solani	*Fusarium solani*
FRAP	ferric reducing antioxidant power
K. marina	*Kocuria marina*
K. pneumoniae	*Klebsiella pneumoniae*
L. fermentum	*Lactobacillus fermentum*
L. maculans	*Leptosphaeria maculans*
L. monocytogenes	*Listeria monocytogenes*
LP	lipid peroxidation
M. canis	*Microscopium canis*
M. luteus	*Micrococcus luteus*
NO	nitric oxide
P. aeruginosa	*Pseudomonas aeruginosa*
P. chrysogenum	*Penicillium chrysogenum*
P. cyclopium	*Penicillium cyclopium*
P. expansum	*Penicillium expansum*
P. fluorescens	*Pseudomonas fluorescens*
P. italicum	*Penicillium italicum*

P. mirabilis	*Proteus mirabilis*
P. putida	*Pseudomonas putida*
P. savastanoi	*Pseudomonas savastanoi*
P. vulgaris	*Proteus vulgaris*
R. solani	*Rhizoctonia solani*
S. aureus	*Staphylococcus aureus*
S. enterica	*Salmonella enterica*
S. enteritidis	*Salmonella enteritidis*
S. gallinarum	*Salmonella gallinarum*
S. mutans	*Streptococcus mutans*
S. pyogenes	*Streptococcus pyogenes*
S. salivarius	*Streptococcus salivarius*
S. sanguis	*Streptococcus sanguis*
S. sclerotiorum	*Sclerotinia sclerotiorum*
S. simulans	*Staphylococcus simulans*
S. sobrinus	*Streptococcus sobrinus*
S. typhimurium	*Salmonella typhimurium*
T. mentagrophytes	*Trichophyton mentagrophytes*
X. vesicatoria	*Xanthomonas vesicatoria*
Y. enterocolitica	*Yersinia enterocolitica*

17.1 Introduction

Essential oils are high-valued plant metabolites widely incorporated into food, cosmetics, and pharmaceutics. They are usually utilized as fragrance chemicals; however, they are important active ingredients due to their biological potential. Examples of highly valued essential oils used as fragrances are rose, citrus, lavender, and other oils obtained from Lamiaceae family plants (Sharmeen et al. 2021). In industrial conditions, steam distillation is used to isolate essential oils. Hydrolates (or hydrosols, floral waters, distillates) are the by-product of this process. They are water solutions of volatile compounds collected in Florentine flask together with the essential oil (Aćimović et al. 2020).

There is growing interest to turn this aromatic by-product into a value-added product, in order to decrease waste material of processing medicinal plants. The fact that the ratio between the primary product of distillation (essential oil) and the by-product (hydrolate) is very low (Elguea-Culebras et al. 2022) and that the by-product is free of production cost is valuable commercially. The main cost is adequate packaging and storage to reduce secondary contamination and to preserve quality (Alavi et al. 2017).

The overall experience indicates that hydrolates are an important source of relevant phytochemicals with significant pharmacological potential (Politi et al. 2022). Nowadays, hydrolates are used in soft drinks (Hamedi et al. 2017),

aromatherapy products (Abdullah and Moosa 2010), and cosmetics (Jakubczyk et al. 2021). However, there are many studies which indicate that they have potential uses in food processing as sanitizing agents of fresh fruits and vegetables (Tornuk et al. 2011, 2014; Sagdic et al. 2013; Tornuk and Dertli 2015; Ozturk et al. 2016; Xylia et al. 2019; Xiao et al. 2020; Irkin et al. 2021), or as biosanitizers to control biofilms on different surfaces in food industry (Chorianopoilos et al. 2008; Rossi et al. 2022).

Furthermore, in organic agriculture hydrolates have great potential to be used as insecticides (Finetti et al. 2022), nematicides (Julio et al. 2017; Pardavella et al. 2020; Andres et al. 2018), and fungicides (Boyraz and Ozcan 2006; Moon et al. 2007; Paramalingam et al. 2021; Tabti et al. 2014; Zatla et al. 2017, 2020). Further research of hydrolates needs to be focused on valorization through development of novel natural formulations as alternative products to commercial applications in ecologically sustainable agriculture (Mihai et al. 2022).

Despite the current popularity of hydrolates and their multiple applications, especially as natural pesticides, it is necessary to evaluate their environmental risks (Pino-Oto et al. 2022). However, all hydrolates did not express biological activity (Carlini et al. 1983), mainly because they contain less than 1 g/L (i.e., 0.1%) of water-soluble volatile compounds (Aćimović et al. 2020).

Due to circular economy, there is an increased interest in the essential oil industry by-products such as hydrolates (Elguea-Culebras et al. 2022). Hydrolates have attracted a great interest among the scientific community in the past two decades (Zekri et al. 2022). There are several review papers with lists of studied hydrolates, their chemical composition, and biological activities (Tavares et al. 2022; Al-Mansour 2021; D'Amato et al. 2018). This scientific group, composed of agronomists, technologists, and chemists started investigations related to this topic in 2020 (Aćimović et al. 2020). Since then, the chemical composition and activities of different hydrolates were investigated: *Dracocephalum moldavica* (Aćimović et al. 2022a), *Lavandula* × *intermedia* (Aćimović et al. 2022b), *Artemisia annua* (Aćimović et al. 2022c), *Thymus vulgaris* (Konstantinović et al. 2022), and many others (research in progress).

17.2 Hydrolate Production

Steam distillation is the most frequently used technique for essential oil production under industrial conditions. Plant material is loaded into a distillation tank and subjected to steam under pressure. The steam comes out through plant material, collects volatile compounds, passes through a condenser and cooler, and is collected in a Florentine flask. Essential oil mainly contains water-insoluble compounds which float on the surface. However, some volatile compounds are water soluble, and they remain dissolved in water, and this mixture (suspension) is called hydrolate. Because of this, hydrolates are aromatic and mild and have a pleasant scent (Aćimović et al. 2020, 2022d).

Extraction of water-soluble volatile constituents from hydrolates can be done by simultaneous distillation-extraction (SDE) by Likens-Nickerson apparatus (Eikani et al. 2005; Aćimović et al. 2022a, b, c), as well as the purge and trap technique (P&T), liquid-liquid extraction (LLE), solid-phase extraction (SPE), solid-phase microextraction (SPME), or headspace solid-phase microextraction (HS-SPME) (Paolini et al. 2008; Smigielski et al. 2013; Erbas and Baydar 2016; Canbay 2017; Belkamel et al. 2018).

Hydrolates were mostly obtained from species belonging to the Lamiaceae family (Tavares et al. 2022). This chapter includes chemical compositions and biological activities of hydrolates obtained from the most important plants from this family. These plants are widely used for essential oil extraction and have large-scale application in different industries and include lavender, thyme, oregano, savory, mint, sage, and rosemary. Furthermore, rose essential oil and hydrolate are probably the most studied of all and the only one that has a valorized application for obtaining secondary oil (Ayci et al. 2005). In addition, citrus and bay laurel are very popular plants for essential oil extraction. Their hydrolates are interesting to investigate because their odor and taste are similar to that plant or corresponding essential oil (Jain and Mishra 2012). Figure 17.1 illustrates the plant species (together with the family and plant part used for essential oil distillation) which we covered in this book chapter.

17.3 Lavender Hydrolate

There are many lavender species, but only two are commercially important as essential oil-bearing plants: true or English lavender (*Lavandula angustifolia*) and hybrid lavender commonly known as lavandin (*Lavandula* × *intermedia*). The main compounds in both species of lavender essential oils are linalool which gives a floral, citric, fresh, and sweet odor and linalyl acetate which has very similar odor properties to linalool (Elsharif et al. 2015). Lavender essential oil is popular as a complementary medicine and antimicrobial and antioxidant agent. It is used against stress and depression and as an additive to food flavoring, pharmaceuticals, perfumery, and cosmetic products, as well as in aromatherapy because of its higher linalool and linalyl acetate content. Lavandin essential oil is usually utilized in industrial and domestic cleaning products, hygiene products, and detergents owing to the higher camphor levels (Cavanagh and Wilkinson 2005; Rathore and Kumar 2022). Lavender and lavandin hydrolates have characteristic odors similar to the essential oil. They mainly contain linalool (7.7–55.6%) and other oxygenated monoterpenes, but not linalyl acetate or other sesquiterpenes which are present in the essential oil (Aćimović et al. 2022b). The chemical composition of lavender hydrolate is well studied, and a brief review is given in Table 17.1.

Biological activities of lavender hydrolates according to literature is given in Table 17.2. As it can be seen, the antioxidant activity of lavender hydrolate (Aazza et al. 2011; Prusinowska et al. 2013; Kalemba-Drozdz and Cierniak 2019), as well as

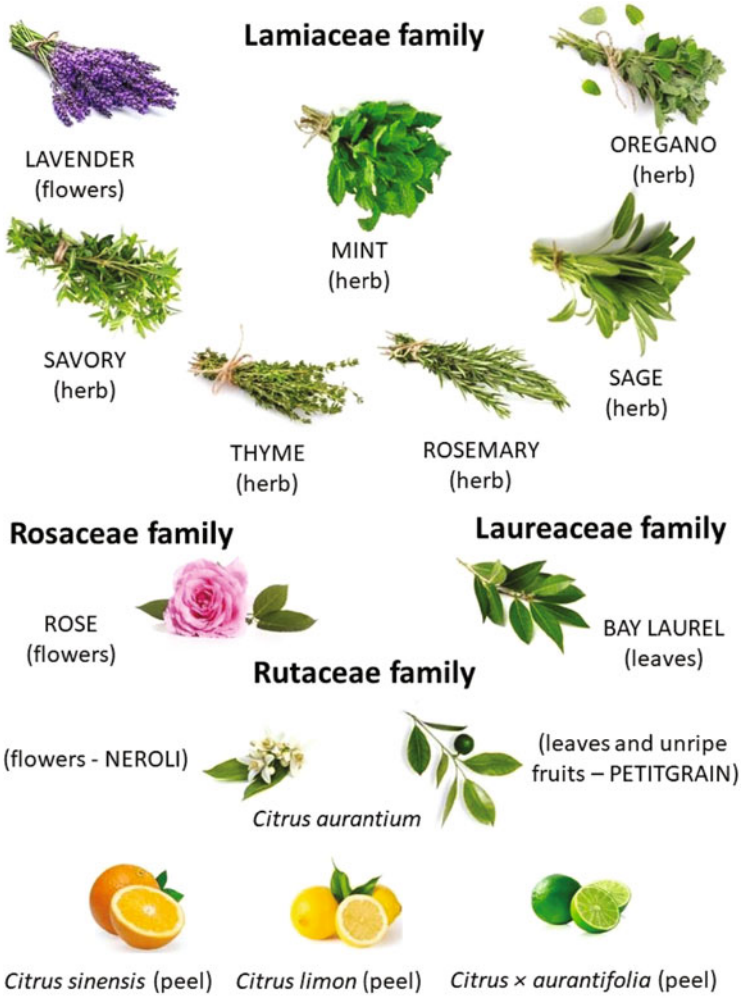

Fig. 17.1 Plant species commonly used for essential oil and hydrolate production

the antimicrobial activity (Moon et al. 2007; Inouye et al. 2009; Prusinowska et al. 2013; Kunicka-Styczynska et al. 2014; Garzoli et al. 2020), is mainly low. However, investigations demonstrate that concentrated hydrolates showed significant antimicrobial activity, while non-concentrated hydrolates significantly reduced biofilm formation (Šilha et al. 2020). Additionally, data shows that the minimum inhibitory concentration for essential oil is lower than for the corresponding hydrolate, and the volatile organic compound in hydrolate is effective (Vito et al. 2021). Furthermore, lavender hydrolate exhibits nematicide, repellency, and allelopathic activities, thus making them very interesting for organic agriculture (Andres et al. 2018; Politi et al. 2020).

Table 17.1 *Lavandula* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Lavandula angustifolia	Linalool (26.5%)	Smigielski et al. (2013)
Lavandula angustifolia	Linalool (29.0–39.2%), α-terpineol (7.1–12.7%)	Prusinowska et al. (2013)
Lavandula angustifolia	Linalool (24.2–39.2%), linalool oxide (18.3–25.0%), α-terpineol (6.5–12.7%), borneol (5.8–14.3%)	Prusinowska and Smigielski (2015)
Lavandula angustifolia	Linalool (25.7–44.9%), α-terpineol (4.1–8.5%), borneol (4.0–6.0%), terpinene-4-ol (3.7–5.4%)	Prusinowska and Smigielski (2015)
Lavandula angustifolia	1,8-Cineole (20.6%), cis-linalool oxide (11.9%), α-terpineol (10.4%), trans-linalool oxide (9.1%), linalool (7.9%), 2,6-dimethyl-3,7-octadiene-2,6-diol (5.9%), neodihydrocarveol (5.9%)	Šilha et al. (2020)
Lavandula angustifolia	Linalool (29.0%), coumarin (15.5%), α-terpineol (14.2%), caryophyllene oxide (9.8%), linalool oxide (6.9%), linalyl acetate (6.5%), trans-linalool oxide (6.0%)	Gaspar-Pintiliescu et al. (2022)
Lavandula angustifolia	1,8-Cineole (20.8%), linalool (22.5%), camphor (16.9%), endo-borneol (6.6%), terpinene-4-ol (7.9%), linalyl acetate (5.7%)	Popa et al. (2021)
Lavandula angustifolia	Linalool (42.9%), camphor (18.4%), α-terpineol (12.6%), 1,8-cineole (11.8%), terpinene-4-ol (8.4%), borneol (5.8%)	Garzoli et al. (2021)
Lavandula angustifolia	Linalool (45.0%), camphor (15.7%), 1,8-cineole (14.8), α-terpineol (11.8%), borneol (11.3%)	Aazza et al. (2011)
Lavandula intermedia	Borneol (31.8%), linalool (19.9%), camphor (17.5%), α-terpineol (10.1%)	Moon et al. (2007)
Lavandula intermedia	α-Terpineol (24.0%), linalool (19.0%), terpinene-4-ol (14.0%)	Moon et al. (2007)
Lavandula intermedia	Linalool (55.6%), borneol (13.5%), camphor (13.4%)	Baydar and Kineci (2009)
Lavandula intermedia	Linalool (33.6%), 1-octen-3-ol (16.5%), terpinene-4-ol (11.3%)	Martinez-Gil et al. (2013)
Lavandula intermedia	α-Terpineol (14.7%), linalool (14.6%), camphor (9.9%), borneol (9.3%), cis-linalool oxide (7.8%), trans-linalool oxide (7.4%), 1,8-cineole (5.0%)	Andres et al. (2018)
Lavandula intermedia	Trans-linalool oxide (31.1%), cis-linalool oxide (29.2%), 1,8-cineole (8.6%), linalool (7.7%), camphor (7.2%)	Pljevljakušić and Drinić (2020)
Lavandula intermedia	1,8-Cineole (52.9%), camphor (19.6%), linalool (12.6%), terpinene-4-ol (5.4%)	Garzoli et al. (2020)
Lavandula intermedia	Linalool (43.8%), 1,8-cineole (25.4%), camphor (12.8%)	Politi et al. (2020)
Lavandula intermedia	Linalool (34.2–47.5%), camphor (2.8–18.8%), borneol (10.0–31.9%), terpinene-4-ol (4.8–11.0%), α-terpineol (1.7–8.7%)	Truzzi et al. (2021)
Lavandula intermedia	1,8-Cineole (24.4%), linalool (29.8%), camphor (9.2%), endo-borneol (13.7%), terpinene-4-ol (10.5%)	Popa et al. (2021)

(continued)

Table 17.1 (continued)

Plant material	Recovery oil	Reference
Lavandula intermedia	Linalool (21.9–32.1%), 1,8-cineole (12.7–26.2%), borneol (10.6–24.4%), terpinene-4-ol (6.4–12.2%), camphor (4.5–7.1%), cis-linalool oxide (1.4–11.5%), α-terpineol (1.4–6.0%), trans-linalool oxide (1.3–10.9%)	Aćimović et al. (2022b)
Lavandula angustifolia	Linalool (42.2%), α-terpineol (19.0%), terpinene-4-ol (20.2%)	Vito et al. (2021)
Lavandula intermedia	1,8-Cineole (19.1%), linalool (34.2%), camphor (22.1%), α-terpineol (5.2%), terpinene-4-ol (7.6%)	Vito et al. (2021)

17.4 Thyme Hydrolate

Thyme is the common name of many taxa belonging to the *Thymus* and *Thymbra* genera (Figueiredo et al. 2010). These plants are economically important due to their medicinal and aromatic properties. However, the genus *Thymus* is taxonomically very complex, with a large number of species distributed throughout the Mediterranean region over Europe, northwest Africa, Ethiopia, Asia, and Greenland. It is characterized by the high variability of morphological and chemical traits (Bartolucci and Domina 2014). Contrastingly, the genus *Thymbra* with their species (*T. spicata*, *T. capitata*, and *T. sintenisii*) has a minor distribution area extending to the Eastern Mediterranean region countries (Kizil et al. 2015). Thyme and its essential oil have a strong rich herbaceous fragrance, derived from the main volatile compound thymol and its isomer carvacrol. Thyme essential oil possesses high biological activity and is used in food and pharmaceutical industries (Meeran et al. 2017; Nieto 2020). The chemical composition of *Thymus* sp. and *Thymbra* sp. recovery essential oil from hydrolate is shown in Table 17.3. As can it be seen, the main compounds are thymol and carvacrol, followed by 1,8-cineole, linalool, geraniol, α-terpineol, etc.

According to a review of biological activity of *Thymus* sp. and *Thymbra* sp. hydrolates (Table 17.4), it could be said that thyme hydrolates possess significant antimicrobial, antiviral, and nematocidal activities, without toxic effects. It could be widely applied in sanitizing fresh fruits and vegetables (Tornuk et al. 2011, 2014; Sagdic et al. 2013; Tornuk and Dertli 2015; Ozturk et al. 2016). Apart from this, the thyme hydrolate could be used for skin care (Oliveira et al. 2022) and for reduction of chemotherapy-induced oral mucositis (Yayla et al. 2016).

Table 17.2 Biological activity of *Lavandula* sp. hydrolate

Plant material	Activity	Method	Result	Reference
Lavandula spp.	Antimicrobial	*A. nidulans*, *L. maculans*, *S. sclerotiorum*, *T. mentagrophytes*	No activity	Moon et al. (2007)
Lavandula angustifolia	Antimicrobial	*C. albicans*	Moderate inhibition	Inouye et al. (2009)
Lavandula angustifolia	Antimicrobial	*A. niger*, *B. subtilis*, *Candida* sp., *E. coli*, *P. expansum*, *P. aeruginosa*, *S. aureus*	Low activity	Prusinowska et al. (2013)
Lavandula angustifolia	Antimicrobial	*A. niger*, *Candida* sp., *E. coli*, *S. aureus*	No activity	Kunicka-Styczynska et al. (2014)
Lavandula intermedia	Antimicrobial	*E. coli*, *B. cereus*	No activity	Garzoli et al. (2020)
Lavandula angustifolia	Antimicrobial	*A. butzleri*, *A. cryaerophilus*, *A. lanthieri*, *A. skirrowii*, *A. thereius*, *S. aureus*, *E. faecalis*, *P. aeruginosa*, *E. coli*, *C. albicans*	Significant activity	Šilha et al. (2020)
Lavandula angustifolia	Antimicrobial	*Candida* sp., *Trichophyton* sp., *M. canis*, *S. aureus*, *S. pyogenes*, *E. faecalis*, *E. faecium*	Low activity	Vito et al. (2021)
Lavandula intermedia	Antimicrobial	*Candida* sp., *Trichophyton* sp., *M. canis*, *S. aureus*, *S. pyogenes*, *E. faecalis*, *E. faecium*	Low activity	Vito et al. (2021)
Lavandula angustifolia	Antioxidant	ABTS, $\bullet O_2^-$ scavenging assay, •OH scavenging assay	Moderate activity	Aazza et al. (2011)
Lavandula angustifolia	Antioxidant	ORAC, DPPH	Low activity	Prusinowska et al. (2013)
Lavandula angustifolia	Antioxidant	FRAP	Weak activity	Kalemba-Drozdz and Cierniak (2019)
Lavandula intermedia	Nematocide	*Meloidogyne javanica*	Significant activity	Andres et al. (2018)
Lavandula intermedia	Insecticide	*Tribolium confusum*	Good repellency	Politi et al. (2020)
Lavandula intermedia	Herbicide	*Raphanus sativus*	Inhibited seed germination	Politi et al. (2020)

17.5 Oregano Hydrolate

The genus *Origanum* consists of aromatic and medicinal plants; it is characterized by morphological and chemical diversity and distributed around the Mediterranean area, Eurasia, and North Africa (García-Beltrán and Esteban 2016). The most important species from this genus from agricultural and industrial standpoint are

Table 17.3 *Thymus* sp. and *Thymbra* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Thymus capitatus	Carvacrol (95.1%)	Tabti et al. (2014)
Thymus citriodorus	1,8-Cineole (26.6%), linalool (24.5%), geraniol (14.1%), α-terpineol (11.4%), thymol (9.2%)	Oliveira et al. (2022)
Thymus glandulosus	Carvacrol (46.0%), thymol (44.7%)	Moukhles et al. (2018)
Thymus mastichina	Thymol (98.6%)	Kessler et al. (2022)
Thymus munbyanus	Carvacrol (36.9%), linalyl anthranilate (15.8%), borneol (10.2%), camphor (5.4%)	Moukhles et al. (2018)
Thymus pannonicus	Geranial (37.9%), neral (27.7%)	Popa et al. (2021)
Thymus vulgaris	Carvacrol (93.3%)	Aazza et al. (2011)
Thymus vulgaris	Carvacrol (35.7%), *o*-cymene (8.0%), thymol (7.0%), linalool (5.5%), carvacrol methyl ether (5.2%)	Sagdic et al. (2013)
Thymus vulgaris	Thymol (98.1%)	Hay et al. (2018)
Thymus vulgaris	Thymol (77.1%), linalool (7.0%)	Andres et al. (2018)
Thymus vulgaris	Thymol (63.0%), carvacrol (21.5%)	Popa et al. (2021)
Thymus vulgaris	Thymol (76.3%), borneol (7.1%)	Konstantinović et al. (2022)
Thymus zygis	Thymol (61.9%), borneol (8.5%), carvacrol (6.4%)	Andres et al. (2018)
Thymbra capitata	Carvacrol (75.1%), 4-*tert*-buthyl catechol (14.7%)	Moukhles et al. (2018)
Thymbra capitata	Carvacrol (78.0–82.2%), *p*-cymene (3.8–6.0%), γ-terpinene (3.5–5.7%)	Moukhles et al. (2019)
Thymbra capitata	Carvacrol (98.1%)	Ferraz et al. (2022)

O. compactum, *O. hirtum*, *O. majorana*, *O. onites*, and *O. vulgare*. Oregano essential oil is widely popular for its pleasant odor. It has also gained considerable attention because of its antioxidant and antimicrobial activities, mainly contributed to the presence of carvacrol and thymol (Plati et al. 2021). In the food industry, oregano essential oil is used as a bio-preservation compound, while in the pharmaceutical industry, it is a component used in preparations for treating respiratory tract disorders, painful menstruation, rheumatoid arthritis, dyspepsia, and urinary tract disorders, as well as many others (Kamaneh et al. 2020). As it can be seen from Table 17.5, the main compounds of oregano recovery essential oil from hydrolate are the same as in the essential oil: carvacrol and thymol. However, it is known that

Table 17.4 Biological activity of *Thymus* sp. and *Thymbra* sp. hydrolates

Plant material	Activity	Method	Result	Reference
Thymus capitatus	Antimicrobial	*A. niger*, *A. oryza*, *P. italicum*, *F. solani*	Strong activity	Tabti et al. (2014)
Thymus citriodorus	Antimicrobial	*C. acnes*	Significant activity	Oliveira et al. (2022)
Thymus citriodorus	Anti-inflammatory	Ability to inhibit NO production in stimulated macrophages	Significant activity	Oliveira et al. (2022)
Thymus citriodorus	Antioxidant	NO scavenging activity, DPPH	Poor activity	Oliveira et al. (2022)
Thymus citriodorus	Toxicity	*Daphnia manga*	Nontoxic	Oliveira et al. (2022)
Thymus glandulosus	Antimicrobial	*E. coli*, *P. mirabilis*, *B. subtilis*, *S. aureus*	Great activity	Moukhles et al. (2018)
Thymus munbyanus	Antimicrobial	*E. coli*, *P. mirabilis*, *B. subtilis*, *S. aureus*	Great activity	Moukhles et al. (2018)
Thymus serpyllum	Antimicrobial	*A. hydrophila*, *E. coli*, *P. aeruginosa*, *P. fluorescens*	High activity	Oral et al. (2008)
Thymus vulgaris	Antimicrobial	*E. coli*, *S. aureus*, *Y. enterocolitica*	Slight activity	Sagdic (2003)
Thymus serpyllum	Antimicrobial	*E. coli*, *S. aureus*, *Y. enterocolitica*	Slight activity	Sagdic (2003)
Thymus vulgaris	Antioxidant activity	ABTS, $\bullet O_2^-$ scavenging assay, •OH scavenging assay	High activity	Aazza et al. (2011)
Thymus vulgaris	Antimicrobial	*E. coli*, *S. typhimurium*	Significant activity	Tornuk et al. (2011)
Thymus vulgaris	Antimicrobial	*E. coli*	Significant activity	Sagdic et al. (2013)
Thymus vulgaris	Antimicrobial	*S. aureus*	Significant activity	Tornuk et al. (2014)
Thymus vulgaris	Antimicrobial	*E. coli*, *S. aureus*	Significant activity	Tornuk and Dertli (2015)
Thymus vulgaris	Antimicrobial	Natural mycobiota on the surface of sucuk	No activity	Ozturk (2015)
Thymus vulgaris	Antimicrobial	*S. typhimurium*, *L. monocytogenes*, *E. coli*	Significant activity	Ozturk et al. (2016)
Thymus vulgaris	Reduction of chemotherapy-induced oral mucositis	Oral rinse	Promising results in alleviating oral mucositis	Yayla et al. (2016)
Thymus vulgaris	Antiviral	Porcine reproductive and respiratory syndrome virus	Significant activity	Kaewprom et al. (2017)
Thymus vulgaris	Antimicrobial	*E. coli*, *P. aeruginosa*, *S. aureus*, *C. albicans*, *A. niger*	Significant activity	Hay et al. (2018)

(continued)

Table 17.4 (continued)

Plant material	Activity	Method	Result	Reference
Thymus vulgaris	Antioxidant	ABTS	High activity	Hay et al. (2018)
Thymus vulgaris	Nematocide	*Meloidogyne javanica*	Significant activity	Andres et al. (2018)
Thymus zygis	Nematocide	*Meloidogyne javanica*	Significant activity	Andres et al. (2018)
Thymbra spicata	Antimicrobial	*B. subtilis*, *S. enteritidis*	High activity	Al-Turki (2007)
Thymbra spicata	Antimicrobial	*B. amyloliquefaciens*, *B. brevis*, *B. cereus*, *E. coli*, *P. vulgaris*, *S. enteritidis*, *S. gallinarum*, *S. aureus*, *Y. enterocolitica*	Significant activity	Sagdic and Ozcan (2003)
Thymbra capitata	Antimicrobial	*S. typhimurium*	Antibiofilm activity	Karampoula et al. (2016)
Thymbra capitata	Antimicrobial	*E. coli*, *P. mirabilis*, *B. subtilis*, *S. aureus*	Strong activity	Moukhles et al. (2018)

Table 17.5 *Origanum* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Origanum compactum	Carvacrol (55.0–76.8%), thymol (19.5–40.6%)	Jeannot et al. (2003)
Origanum compactum	Carvacrol (75.4–76.8%), thymol (19.3–19.6%)	Belkamel et al. (2018)
Origanum hirtum	Thymol (100%)	Vito et al. (2021)
Origanum majorana	Terpinene-4-ol (70.7%)	Aazza et al. (2011)
Origanum majorana	Carvacrol (78.0%), terpinene-4-ol (11.3%)	Petrakis et al. (2015)
Origanum onites	Carvacrol (29.9%), thymol (28.3%)	Sagdic et al. (2013)
Origanum vulgare	Thymol (83.4%)	Verma et al. (2012)
Origanum vulgare	Carvacrol (94.7%)	Verma et al. (2012)
Origanum vulgare	Carvacrol (92.5%)	Khan et al. (2018)
Origanum vulgare	1-Octen-3-ol (13.31%), caryophyllene oxide (12.4%), linalool (11.6%), α-terpineol (6.2%), spathulenol (5.6%), 1,8-cineole (5.4%)	Popa et al. (2021)
Origanum vulgare var. *aureum*	Linalool (54.1%), thymol (22.0%)	Popa et al. (2021)

Table 17.6 Biological activity of *Origanum* sp. hydrolates

Plant material	Activity	Method	Result	Reference
Origanum vulgare	Antimicrobial	*B. amyloliquefaciens*, *B. brevis*, *B. cereus*, *B. subtilis* var. *niger*, *E. aerogenes*, *E. coli*, *K. pneumoniae*, *P. vulgaris*, *S. enteritidis*, *S. gallinarum*, *S. typhimurium*, *S. aureus*, *Y. enterocolitica*	High activity	Sagdic and Ozcan (2003)
Origanum vulgare	Antimicrobial	*E. coli*, *S. aureus*, *Y. enterocolitica*	Significant activity	Sagdic (2003)
Origanum onites	Antimicrobial	*E. coli*, *S. aureus*, *Y. enterocolitica*	High activity	Sagdic (2003)
Origanum majorana	Antimicrobial	*E. coli*, *S. aureus*, *Y. enterocolitica*	High activity	Sagdic (2003)
Origanum vulgare	Green olive fermentation	Brine + hydrolate	High sensory activity	Ozcan et al. (2008)
Origanum majorana	Antioxidant	ABTS, $\bullet O_2^-$ scavenging assay, •OH scavenging assay	Moderate activity	Aazza et al. (2011)
Origanum onites	Antimicrobial	*E. coli*	High activity	Sagdic et al. (2013)
Origanum onites	Antimicrobial	*E. coli*, *S. aureus*	Significant activity	Tornuk and Dertli (2015)
Origanum majorana	Insecticide	*Myzus persicae*	Strong activity	Petrakis et al. (2015)
Origanum onites	Antimicrobial	*S. typhimurium*, *L. monocytogenes*, *E. coli*	High activity	Ozturk et al. (2016)
Origanum vulgare	Antimicrobial	*E. coli*, *P. aeruginosa*, *S. aureus*, *M. luteus*	Significant activity	Khan et al. (2018)
Origanum majorana	Antioxidant	LP (TBARS)	High activity	Xylia et al. (2019)
Origanum majorana	Antimicrobial	Total viable counts of yeast and filamentous fungi	High activity	Xylia et al. (2019)
Origanum hirtum	Antimicrobial	*Candida* sp., *Trichophyton* sp., *M. canis*, *S. aureus*, *S. pyogenes*, *E. faecalis*, *E. faecium*	High activity	Vito et al. (2021)

carvacrol and thymol have high volatility and low water solubility and stability (Yildiz et al. 2018; Celebioglu et al. 2018).

A review of biological activities of hydrolates from thyme species is given in Table 17.6. Utilization of thymol and carvacrol in the food and pharmaceutical fields

has recently been limited by its poor water solubility and stability (Zhou et al. 2021). However, excellent results were obtained by applying oregano hydrolates for washing fresh cut fruits and vegetables for decontamination of foodborne pathogens, as very effective natural food sanitizers (Sagdic et al. 2013; Tornuk and Dertli 2015; Ozturk et al. 2016; Xylia et al. 2019). Furthermore, it can be used for green olive fermentation to improve sensory characteristics (Ozcan et al. 2008), as well as for skin care products (Vito et al. 2021).

17.6 Savory Hydrolate

The genus *Satureja* contains about 200 species, mainly distributed in the Mediterranean region but also found in other temperate regions of Europe, West Asia, North Africa, and South America (Satil et al. 2002). *Satureja* sp., commonly known as savorys, are used in traditional medicine, as well as for flavoring food and in pharmaceutical and cosmetic industries (Tepe and Cilkiz 2015). The most important in cultivation are summer savory (*S. hortensis*) and winter savory (*S. montana*) (Kameli et al. 2013), while others are mainly endemic (Aćimović et al. 2021). Chemical compositions of *Satureja* species essential oils are mainly characterized by oxygenated monoterpenes thymol and carvacrol (Tepe and Cilkiz 2015). Similar to thyme and oregano, the main compounds in savory hydrolates are carvacrol and thymol (Table 17.7).

A review of biological activities of savory hydrolates is given in Table 17.8. Results show that it possesses strong antimicrobial properties which can be used as antimicrobial agents to prevent deterioration of food products (Sagdic and Ozcan 2003), for sanitizing fresh cut fruits and vegetables (Sagdic et al. 2013; Ozturk et al. 2016), and as antibiofilm agents on stainless steel (Chorianopoilos et al. 2008). Furthermore, nematocidal activity was also established (Pardavella et al. 2020), as well as activity against plant pathogens (Boyraz and Ozcan 2005, 2006; Proto et al. 2022).

Table 17.7 *Satureja* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Satureja hellenica	Carvacrol (50.1%), borneol (20.4%), terpinene-4-ol (6.7%)	Pardavella et al. (2020)
Satureja hortensis	Carvacrol (24.7%), thymol (14.7%), *o*-cymene (11.1%)	Sagdic et al. (2013)
Satureja montana	Carvacrol (85.8%), thymol (13.9%)	Vito et al. (2021)

Table 17.8 Biological activity of *Satureja* sp. hydrolates

Plant material	Activity	Method	Result	Reference
Satureja hortensis	Antimicrobial	*A. mali*, *B. cinerea*, *S. sclerotiorum*, *C. circinans*	Significant activity	Boyraz and Ozcan (2006)
Satureja hortensis	Antimicrobial	*R. solani*, *F. oxysporum* f. sp. *tulipae*, *B. cinerea*, *A. citri*	Significant activity	Boyraz and Ozcan (2005)
Satureja hortensis	Antimicrobial	*B. amyloliquefaciens*, *B. brevis*, *B. cereus*, *B. subtilis* var. *niger*, *E. aerogenes*, *E. coli*, *K. pneumoniae*, *P. vulgaris*, *S. enteritidis*, *S. gallinarum*, *S. typhimurium*, *S. aureus*, *Y. enterocolitica*	Significant activity	Sagdic and Ozcan (2003)
Satureja thymbra	Antimicrobial	*S. simulans*, *L. fermentum*, *P. putida*, *S. enterica*, *L. monocytogenes*	Antibiofilm activity	Chorianopoilos et al. (2008)
Satureja hortensis	Antimicrobial	*E. coli*	Significant activity	Sagdic et al. (2013)
Satureja hortensis	Antimicrobial	*S. typhimurium*, *L. monocytogenes*, *E. coli*	High activity	Ozturk et al. (2016)
Satureja hellenica	Nematocide	*Meloidogyne incognita*, *Meloidogyne javanica*	Significant activity	Pardavella et al. (2020)
Satureja montana	Antimicrobial	*Candida* sp., *Trichophyton* sp., *M. canis*, *S. aureus*, *S. pyogenes*, *E. faecalis*, *E. faecium*	Significant activity	Vito et al. (2021)
Satureja montana	Eco-toxicity	*Daphna magna*, *Vibrio fischeri*, *Eisenia fetida*	High eco-toxicity	Pino-Oto et al. (2022)
Satureja montana	Antimicrobial	*E. amylovora*, *X. vesicatoria*, *A. vitis*, *P. savastanoi* ssp. *savastanoi*	Significant activity	Proto et al. (2022)

17.7 Mint Hydrolate

Mentha species, commonly known as mints, with many species and hybrids, grow on all five continents (Kokkini 1991). Mints are one of the most economically important essential oil-bearing crops widely used in industry, as fresh or dried plant materials for flavoring food, pharmaceuticals, cosmetics, etc. (Tafrihi et al. 2021). They are also popular because of many beneficial effects and widely consumed as tea infusions, extracts, or essential oils in traditional medicine, as well as in everyday nutrition for treatment or prevention of various disorders and conditions, such as biliary disorders, menstrual cramps, stomach pain, constipation, gingivitis, and toothache. These are treated with the decoction of spearmint leaves; leaves are also used as a poultice to relieve rheumatism and combat fever (Brahmi et al. 2017). The chemical composition of essential oil depends on the species, as does the chemical composition of the hydrolate (Table 17.9).

Table 17.9 *Mentha* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Mentha arvensis	Menthol (75.8%), menthone (10.8%)	Ohtsu et al. (2018)
Mentha crispa	Piperitenone (29.9%), pulegone (13.9%), 1,8-cineole (10.5%)	Wojcik-Stopczynska and Jakowienko (2012)
Mentha longifolia	Pulegone (60.2%), 1,8-cineole (7.9%), isomenthone (7.2%), menthone (6.4%), chrysanthenone (6.4%)	Diop et al. (2016)
Mentha piperita	Menthol (22.1%), menthone (13.6%), 1,8-cineole (6.7%)	Edris (2009)
Mentha piperita	Menthol (69.4%)	Garneau et al. (2014)
Mentha pulegium	Carvacrol (39.4%), piperitenone (10.1%)	Zekri et al. (2014)
Mentha pulegium	Piperitone (97.9%)	Petrakis et al. (2015)
Mentha spicata	Carvone (56.2%), limonene (6.7%)	Edris (2009)
Mentha spicata	1,8-Cineole (22.9%), camphor (13.5%), α-pinene (5.9%)	Zekri et al. (2014)
Mentha spicata	Piperitenone (38.3%), carvone (22.1%), pulegone (14.8%), 1,8-cineole (9.7%)	Ghavidel et al. (2018)
Mentha suaveolens	Piperitone oxide (69.3%)	Zekri et al. (2014)

A review of biological activities of mint hydrolates is given in Table 17.10. Results show that the hydrolate obtained from *M. arvensis* expresses excellent antimicrobial activity against *E. coli* and *S. aureus*, while *M. crispa* shows weak antimicrobial activity against *A. fumigatus*, *A. parasiticus*, *B. cinerea*, *C. herbarum*, *F. oxysporum*, and *P. cyclopium* (Ohtsu et al. 2018; Wojcik-Stopczynska and Jakowienko 2012). *M. piperita* hydrolate possesses high antibacterial activity and shows promising results in alleviating oral mucositis induced by chemotherapy and lessens hot flush annoyance in women being treated for breast cancer (Al-Turki 2007; Dyer et al. 2008; Yayla et al. 2016). *M. pulegium* and *M. suaveolens* show promising insecticidal and antibacterial activities (Petrakis et al. 2015; Zekri et al. 2016, 2022). *M. spicata* express promising antibacterial and herbicidal activity (Zekri et al. 2022; Irkin et al. 2021; Ozkan and Tuncturk 2021).

17.8 Sage Hydrolate

Salvia is an important genus consisting of many species, used for ornamental, medicinal, and aromatic purposes, but only two have commercial importance: common sage (*S. officinalis*) and clary sage (*S. sclarea*) (Damyanova et al. 2016;

Table 17.10 Biological activity of *Mentha* sp. hydrolates

Plant material	Activity	Method	Result	Reference
Mentha arvensis	Antimicrobial	*E. coli*, *S. aureus*	Excellent activity	Ohtsu et al. (2018)
Mentha crispa	Antimicrobial	*A. fumigatus*, *A. parasiticus*, *B. cinerea*, *C. herbarum*, *F. oxysporum*, *P. cyclopium*	Weak activity	Wojcik-Stopczynska and Jakowienko (2012)
Mentha piperita	Antimicrobial	*B. subtilis*, *S. enteritidis*	High activity	Al-Turki (2007)
Mentha piperita	Hot flushes in women being treated for breast cancer	Sprayed on face, arms, hands, neck, or upper chest whenever they felt a hot flush coming on	Lessen hot flush annoyance	Dyer et al. (2008)
Mentha piperita	Reduction chemotherapy-induced oral mucositis	Oral rinse	Promising results in alleviating oral mucositis	Yayla et al. (2016)
Mentha pulegium	Insecticide	*Myzus persicae*	Strong activity	Petrakis et al. (2015)
Mentha pulegium	Insecticide	*Toxoptera aurantii*	High activity	Zekri et al. (2016)
Mentha pulegium	Antimicrobial	*S. aureus*, *E. coli*, *P. aeruginosa*, *P. putida*, *P. mirabilis*	Promising activity	Zekri et al. (2022)
Mentha spicata	Antimicrobial	*S. aureus*, *E. coli*, *P. aeruginosa*, *P. putida*, *P. mirabilis*	Promising activity	Zekri et al. (2022)
Mentha spicata	Antimicrobial	*E. coli*, total microbial counts	Significant activity	Irkin et al. (2021)
Mentha spicata	Herbicide	*Amaranthus retroflexus*	Potential activity	Ozkan and Tuncturk (2021)
Mentha suaveolens	Antimicrobial	*S. aureus*, *E. coli*, *P. aeruginosa*, *P. putida*, *P. mirabilis*	Promising activity	Zekri et al. (2022)
Mentha suaveolens	Insecticide	*Toxoptera aurantii*	High activity	Zekri et al. (2016)

Jasicka-Misiak et al. 2018). *S. officinalis* is one of the most widely used sources for essential oil used in food industry because of its significant health benefits, as well as strong antioxidant and antimicrobial potential in meat processing (Šojić et al. 2021). Furthermore, sage essential oil is used for treating colds, tuberculosis, bronchitis, gastrointestinal diseases, and inflammation and presents antibacterial, antifungal, antitumor, and antioxidant properties (Mot et al. 2022). *S. sclarea* essential oil is widely used in perfumery as a source of fragrance with refreshing and long-lasting

Table 17.11 *Salvia* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Salvia officinalis	Camphor (51.0%), 1,8-cineole (24.0%), β-thujone (12.9%)	Aazza et al. (2011)
Salvia officinalis	Camphor (43.4%), 1,8-cineole (24.0%), cis-thujone (15.5%)	Baydar et al. (2013)
Salvia officinalis	1,8-Cineole (61.4%), camphor (22.5%), α-thujone (8.4%)	Ovidi et al. (2021)
Salvia officinalis	1,8-Cineole (42.9%), α-thujone (24.3%), β-thujone (14.7%), camphor (8.9%)	Politi et al. (2022)
Salvia officinalis	Camphor (81.6%), thujone (15.0%)	Gaspar-Pintiliescu et al. (2022)
Salvia sclarea	Linalool (62.5%), α-terpineol (20.6%)	Verma (2010)
Salvia sclarea	Linalool (89.5%), α-terpineol (10.5%)	Ovidi et al. (2021)

note and aromatherapy as an anxiolytic, against panic attacks, for regulating menstrual cycle and for controlling high blood pressure (Aćimović et al. 2018; Aćimović 2021). Sages are typically cultivated in temperate climatic areas, and different chemotypes have been described in relation to essential oil composition. However, literature review shows that the main compounds in hydrolate are camphor and 1,8-cineole for *S. officinalis* and linalool and α-terpineol for *S. sclarea* (Table 17.11).

The biological activities of sage hydrolates according to literature are given in Table 17.12. According to this review, *S. officinalis* hydrolate shows significant antimicrobial activity and therefore could be used for decontamination of food-borne pathogens in fresh cut fruits and vegetables (Tornuk et al. 2014, 2011; Tornuk and Dertli 2015; Ozturk et al. 2016), while antioxidant activity is low (Aazza et al. 2011; Ovidi et al. 2021). However, it shows promising results in alleviating oral mucositis induced by chemotherapy (Yayla et al. 2016). Contrastingly, *S. sclarea* hydrolate did not show antimicrobial activity, while antioxidant activity was low (Ovidi et al. 2021).

17.9 Rosemary Hydrolate

Rosemary (*Rosmarinus officinalis*) is a highly appreciated plant in food and drink industries due to its distinct organoleptic properties (Christopoulou et al. 2021). In medicine and pharmacy, it is used because of its significant antimicrobial, anti-inflammatory, antioxidant, antiapoptotic, antitumorigenic, antinociceptive, and neuroprotective properties (Ghasemzadeh Rahbardar and Hosseinzadeh 2020). It is a typical Mediterranean plant and the chemical composition of its essential oil depends on the chemotype, as well as growing conditions (Hussain et al. 2010).

Table 17.12 Biological activity of *Salvia* sp. hydrolates

Plant material	Activity	Method	Result	Reference
Salvia officinalis	Antimicrobial	*E. coli* and *S. typhimurium*	Significant activity	Tornuk et al. (2011)
Salvia officinalis	Antimicrobial	*S. aureus*	Significant activity	Tornuk et al. (2014)
Salvia officinalis	Antimicrobial	*E. coli*, *S. aureus*	Significant activity	Tornuk and Dertli (2015)
Salvia officinalis	Antimicrobial	*S. typhimurium*, *L. monocytogenes*, *E. coli*	Significant activity	Ozturk et al. (2016)
Salvia officinalis	Antimicrobial	*E. coli*, *P. fluorescens*, *A. bohemicus*, *B. cereus*, *K. marina*	No activity	Ovidi et al. (2021)
Salvia officinalis	Antioxidant	ABTS, $\bullet O_2^-$ scavenging assay, •OH scavenging assay	Low activity	Aazza et al. (2011)
Salvia officinalis	Antioxidant	DPPH, ABTS	Low activity	Ovidi et al. (2021)
Salvia officinalis	Reduction chemotherapy-induced oral mucositis	Oral rinse	Promising results in alleviating oral mucositis	Yayla et al. (2016)
Salvia sclarea	Antimicrobial	*E. coli*, *P. fluorescens*, *A. bohemicus*, *B. cereus*, *K. marina*	No activity	Ovidi et al. (2021)
Salvia sclarea	Antioxidant	DPPH, ABTS	Low activity	Ovidi et al. (2021)

Several chemotypes were reported, with α-pinene, 1,8-cineole, camphor, borneol, verbenone, and bornyl acetate as dominant compounds (Satyal et al. 2017). According to literature review, the main compounds in rosemary hydrolates are verbenone, camphor, and 1,8-cineole (Table 17.13).

The biological activities of rosemary hydrolates according to literature are given in Table 17.14. It successfully reduced microbiological contamination on fresh fruits and vegetables (Tornuk et al. 2011, 2014; Tornuk and Dertli 2015; Ozturk et al. 2016), while some authors reported low antimicrobial activity (Boyraz and Ozcan 2005; Hay et al. 2018), which is probably linked to the chemical composition of hydrolates. However, the antioxidant activity of rosemary hydrolate is low (Aazza et al. 2011; Hay et al. 2018).

Table 17.13 *Rosmarinus officinalis* chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Rosmarinus officinalis	Verbenone (52.2%), camphor (15.3%)	Paolini et al. (2008)
Rosmarinus officinalis	1,8-Cineole (44.3%), verbenone (25.7%), camphor (11.6%)	Aazza et al. (2011)
Rosmarinus officinalis	Camphor (24.9–32.4%), borneol (20.4–27.0%), 1,8-cineole (15.7–22.5%)	Tomi et al. (2016)
Rosmarinus officinalis	Camphor (51.9%), 1,8-cineole (38.2%)	Hay et al. (2018)
Rosmarinus officinalis	1,8-Cineole (47.1%), camphor (5.4%)	Politi et al. (2022)
Rosmarinus officinalis	Camphor (37.5%), verbenone (34.8%), 1,8-cineole (15.4%), borneol (6.0%)	Gaspar-Pintiliescu et al. (2022)

Table 17.14 Biological activity of *Rosmarinus officinalis* hydrolates

Plant material	Activity	Method	Result	Reference
Rosmarinus officinalis	Antimicrobial	*R. solani*, *F. oxysporum* f. sp. *tulipae*, *B. cinerea*, *A. citri*	Low activity	Boyraz and Ozcan (2005)
Rosmarinus officinalis	Antimicrobial	*E. coli*, *S. typhimurium*	Significant activity	Tornuk et al. (2011)
Rosmarinus officinalis	Antimicrobial	*S. aureus*	Significant activity	Tornuk et al. (2014)
Rosmarinus officinalis	Antimicrobial	*E. coli*, *S. aureus*	Significant activity	Tornuk and Dertli (2015)
Rosmarinus officinalis	Antimicrobial	*S. typhimurium*, *L. monocytogenes*, *E. coli*	Significant activity	Ozturk et al. (2016)
Rosmarinus officinalis	Antimicrobial	*E. coli*, *P. aeruginosa*, *S. aureus*, *C. albicans*, *A. niger*	Low activity	Hay et al. (2018)
Rosmarinus officinalis	Antioxidant	ABTS, $\bullet O_2^-$ scavenging assay, •OH scavenging assay	Low activity	Aazza et al. (2011)
Rosmarinus officinalis	Antioxidant	ABTS	No activity	Hay et al. (2018)

17.10 Rose Hydrolate

The main industrial products from oil-bearing Damask rose (*Rosa damascena* Mill.) are rose essential oil and rose water. Rose oil is the most widely used essential oil in perfumery and cosmetic industry (Erbas and Baydar 2016). However, the average oil content in *R. damascena* flowers is quite small, usually between 0.035% and 0.045% (Atanasova et al. 2016; Erbas and Baydar 2016), and the demand for rose oil on the international market is constantly high (Pal 2013), which leads to its high price. In addition, other species (*R. rugosa*, *R. alba*, *R. brunonii*, *R. canina*, and *R. centifolia*) are also introduced in culture for obtaining essential oil, because of the low essential

Table 17.15 *Rosa* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Rosa damascena	Citronellol (47.4%), geraniol (22.6%), *n*-nonadecane (10.8%)	Eikani et al. (2005)
Rosa damascena	Geraniol (30.7%), citronellol (29.4%), phenethyl alcohol (23.7%), nerol (16.2%)	Ulusoy et al. (2009)
Rosa damascena	Phenethyl alcohol (12.0–73.3%), citronellol (2.7–10.3%), geraniol (0–24.0%), dibutyl phthalate (0–18.8%), eugenol (0–17.8%),	Moein et al. (2014)
Rosa damascena	Phenethyl alcohol (25.0%), geraniol (21.2%), citronellol (20.9%), nerol (10.8%)	Labadie et al. (2015)
Rosa damascena	Phenethyl alcohol (77.0%), citronellol (12.7%), eugenol (5.1%),	Hamedi et al. (2017)
Rosa damascena	Citronellol (28.7%), geraniol (16.4%), nerol (10.8%), phenethyl alcohol (5.0%)	Georgieva et al. (2019)
Rosa damascena	Phenethyl alcohol (45.4%), β-citronellol (34.1%), geraniol (12.2%)	Bayhan et al. (2020)
Rosa damascena	Phenethyl alcohol (35.6%), geraniol (27.9%) nerol (12.7%), citronellol (8.3%), eugenol (6.2%)	Erbas and Baydar (2016)
Rosa damascena	Phenethyl alcohol (43.7%), citronellol (18.2%), geraniol (14.8%)	Maruyama et al. (2017)
Rosa damascena	Phenethyl alcohol (36.0%), citronellol (19.2%), geraniol (13.2%), linalool (8.4%), eugenol (6.0%), nerol (5.8%)	Demirbolat et al. (2019)
Rosa damascena (rose water)	Phenethyl alcohol (90.2%)	Lei et al. (2015)
Rosa damascena (rose water)	Phenethyl alcohol (87.9%)	Lei et al. (2015)
Rosa rugosa (rose water)	Phenethyl alcohol (78.7%), citronellol (13.5%), eugenol (5.7%)	Lei et al. (2015)
Rosa alba	Geraniol (36.4%), citronellol (28.7%), nerol (6.1%), phenethyl alcohol (6.0%)	Georgieva et al. (2019)
Rosa brunonii	Eugenol (52.0%), geraniol (13.3%), phenyl ethyl alcohol (9.4%)	Verma et al. (2016)
Rosa canina	Phenethyl alcohol (46.9%), eugenol (28.8%), citronellol (8.3%)	Hamedi et al. (2017)
Rosa centifolia	Phenethyl alcohol (45.6%), citronellol (24.6%), geraniol (11.3%)	Labadie et al. (2015)
Rosa sp.	2,3-Dehydro-1,8-cineole (23.8%), 3-carene (21.3%), 6-methylhept-5-en-2-one (16.3%),	Xiao et al. (2020)

oil content and short flowering season of *R. damascena* (Erbas and Baydar 2016). Taking into account that essential oil in rose is low, there are processes developed for utilization of by-products for better financial gain. The essential oil separated in the Florentine flask after the distillation process is called decanted or direct oil. The water-soluble fraction in the hydrolate is used for redistillation or cohobation for obtaining recovery or indirect oil, known as water oil. Table 17.15 shows the chemical composition of *Rosa* sp. recovery essential oil according to literature.

Table 17.16 Biological activity of *Rosa* sp. hydrolate

Plant material	Activity	Method	Result	Reference
Rosa damascena	Antibacterial in vivo	Hand-rubbing with 3 mL of rose hydrolate	No significant activity	Bayhan et al. (2020)
Rosa damascena	Antimicrobial	*B. subtilis*, *C. violaceum*, *E. carotovora*, *E. coli*, *P. aeruginosa*, *S. aureus*	No activity	Ulusoy et al. (2009)
Rosa damascena	Antimicrobial	*C. albicans*, *S. aureus*	Significant activity	Maruyama et al. (2017)
Rosa damascena	Antimicrobial	*S. mutans*, *S. salivarius*, *S. sanguis*, *S. sobrinus*	No activity	Aliasghari et al. (2017)
Rosa alba	Antioxidant	LP assay, •OH scavenging assay, $\bullet O_2^-$ scavenging assay	Good activity	Georgieva et al. (2019)
Rosa centifolia	Antioxidant	FRAP	Weak activity	Kalemba-Drozdz and Cierniak (2019)
Rosa damascena	Antioxidant	FRAP	Weak activity	Kalemba-Drozdz and Cierniak (2019)
Rosa damascena	Antioxidant	LP assay, •OH scavenging assay, $\bullet O_2^-$ scavenging assay	Good activity	Georgieva et al. (2019)
Rosa sp.	Sedative	Sensory test, autonomic nervous system activity, mood states, salivary amylase activity	No activity	Tomi et al. (2017)
Rosa sp.	Insomnia	3 mL three times/day for 3 weeks	Significant activity	Jahangir et al. (2008)
Rosa damascena	Antidiabetic	Oral consumption for 45 days	Significant activity	Demirbolat et al. (2019)
Rosa damascena	Immuno-modulatory	Neutrophil adhesion	Significant activity	Maruyama et al. (2017)
Rosa sp.	Preservative	Food model system: fresh cut taros	Significant activity	Xiao et al. (2020)

However, these two oils (direct essential oil and indirect essential oil recovered from the hydrolate) are combined and make the final rose oil "*rose otto*." The compositions of the direct and indirect oils are fairly different (the hydrolate contains only dissolved polar components), and this process is used to complete the aromatic profile of rose oil. Residual water, which remains after cohobation, popularly known as rose water, contains mainly phenethyl alcohol (up to 98.2%) which gives its characteristic rose scent (Erbas and Baydar 2016).

Rose hydrolate and rose water is widely used in food and aromatherapy. The review of investigated biological activities is given in Table 17.16. As it can be seen, experiments showed no antimicrobial activity against *B. subtilis*, *C. violaceum*, *E. carotovora*, *E. coli*, *P. aeruginosa*, *S. aureus*, and oral streptococci (*S. mutans*,

S. salivarius, *S. sanguis*, *S. sobrinus*) (Ulusoy et al. 2009; Aliasghari et al. 2017; Bayhan et al. 2020), but inhibited mycelial growth of clinically isolated *C. albicans* and reduced viability of methicillin-resistant *S. aureus* (Maruyama et al. 2017). Some studies suggest that rose hydrolate expressed good antioxidant properties (Georgieva et al. 2019), while others found antioxidant properties to be weak (Kalemba-Drozdz and Cierniak 2019). Investigations show that rose hydrolate does not exhibit sedative effects on humans (Tomi et al. 2017) but improves symptoms of insomnia and has a positive effect on constipation (Jahangir et al. 2008). Furthermore, it exhibits significant protective properties in diabetes mellitus without toxic effect (Demirbolat et al. 2019) as well as anti-inflammatory activity (Maruyama et al. 2017). Rose hydrosol could be used as an anti-browning agent to preserve the quality of fresh cut foods (Xiao et al. 2020).

17.11 Citrus Hydrolate

The most commercially important citrus species are sweet oranges (*Citrus sinensis*) and tangerines (*C. reticulata*), followed by lemons (*C. limon*), limes (*C. aurantifolia*), and other hybrids (*C. clementina*, *C. maxima*, *C. medica*, etc.). Citruses are primarily used for consumption as fresh fruit or for juice production. However, this usage generates a large amount of processing waste material (citrus peel) which could be reused for essential oil extraction, because the essential oil is localized in the pericarp. Citrus essential oil can be extracted from peel, flowers (neroli), and young citrus shoot, buds, and leaves (petitgrain). Neroli oil is obtained from flowers of bitter orange (*C. aurantium*), although this term is also used for oils extracted from other citrus flowers (Palazzolo et al. 2013). Circular economy aims at recovering valuable material directly from waste to enter a new production cycle and to minimize waste generation (Russo et al. 2021). Therefore, by-products of citrus fruits, such as essential oil and hydrolates, are of high economic and medicinal value in food and cosmetic industries (Kamal et al. 2011). The chemical composition of citrus essential oil depends on the extraction method: mechanical pressing, extraction with solvents, distillation, etc. (Arce and Soto 2008). Regardless of plant species, plant part, or extraction technique, the main compound in this type of oil is linalool, unsaturated monoterpene alcohol with a specific odor—light and refreshing—floral-woody, with a faint citrusy note (Kamatou and Viljoen 2008). The chemical composition of recovery essential oil from hydrolate of different *Citrus* spp. according to literature is given in Table 17.17.

Since citrus hydrosols contain dissolved linalool (9.8–68.9%) and other hydrophilic compounds (geranial, nerol, neral, α-terpineol, geraniol, terpinene-4-ol, limonene, etc.), they could be used in aromatherapy to lessen hot flashes in women being treated for breast cancer (Dyer et al. 2008), but also as anti-browning agents in commercial mushroom production because they exerted significant anti-tyrosinase activity (Lante and Tinello 2015). Antimicrobial and antioxidant activities of citrus hydrolates are variable and depend on species. However, dipping treatment with

Table 17.17 *Citrus* sp. chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Citrus aurantifolia	Geranial (18.3%), nerol (15.8%), neral (15.3%), α-terpineol (14.6%), geraniol (13.1%), terpinene-4-ol (5.8%)	Ndiaye et al. (2017)
Citrus aurantium	Linalool (44.1%), α-terpineol (23.7%)	Labadie et al. (2015)
Citrus aurantium	Linalool (16.6%), neryl acetate (6.5%), nerolidol (5.9%)	Degirmenci and Erkurt (2020)
Citrus aurantium	Linalool (13.8–44.1%), α-terpineol (2.6–20.7%), limonene (0.0–46.6%), geraniol (0.0–26.6%), methyl anthranilate (0.0–11.8%), 1,8-cineole (0.0–15.9%)	Monsef-Esfahani et al. (2004)
Citrus aurantium	Linalool (36.7%), α-terpineol (29.4%), methyl anthranilate (11.3%), nerol (8.8%), indole (5.5%)	Hamedi et al. (2017)
Citrus aurantium	Linalool (47.7%), terpinolene (24.8%), α-terpineol (13.8%), geraniol (6.4%)	Vito et al. (2017)
Citrus aurantium	Linalyl acetate (46.7%), linalool (32.7%)	Edris (2009)
Citrus aurantium	Linalool (47.7%), terpinolene (24.8%), α-terpineol (13.8%), geraniol (6.4%)	Proto et al. (2022)
Citrus clementina	Linalool (68.9%), terpinene-4-ol (12.4%), limonene (6.5%), trans-β-ocimene (6.3%)	Paolini et al. (2008)
Citrus limon	Geraniol (37.5%), α-terpineol (23.3%), citral (22.4%), terpinolene (7.6%), terpinene-4-ol (5.6%)	Lante and Tinello (2015)
Citrus maxima	Trans-linalool oxide (21.3%), α-terpineol (13.0%), cis-linalool oxide (10.3%), linalool (9.8%), geraniol (6.8%), neral (5.9%)	Ndiaye et al. (2017)
Citrus medica	Citral (28.9%), α-terpineol (27.9%), geraniol (25.5%), terpinolene (9.3%)	Lante and Tinello (2015)
Citrus reticulata	Linalool (17.5%), citronellol (16.4%), trans-carveol (12.2%), α-terpineol (10.1%),	Ndiaye et al. (2017)
Citrus sinensis	Terpinolene (63.2%), α-terpineol (22.5%)	Lante and Tinello (2015)
Citrus sinensis	Linalool (34.8%), α-terpineol (9.5%), citronellol (8.4%), limonene-10-ol (9.5%)	Ndiaye et al. (2017)

lemon peel hydrolate washing solution for salad vegetables (lettuce, parsley, and dill) caused decreases in total microbial counts (Irkin et al. 2021), as well as biological control of fusarium wilt of banana (Paramalingam et al. 2021). A review of biological activities of citrus hydrolates is given in Table 17.18.

17.12 Bay Laurel Hydrolate

Laurus nobilis, popularly known as bay laurel, is a tree belonging to the Lauraceae family, native to Asia. It is widely used in food industry due to its flavor, antioxidant, and preservative properties (Saparin et al. 2020; Ordoudi et al. 2022). Bay laurel is

Table 17.18 Biological activity of *Citrus* sp. hydrolate

Plant material	Activity	Method	Result	Reference
Citrus aurantium	Hot flushes in women being treated for breast cancer	Sprayed on face, arms, hands, neck, or upper chest whenever they felt a hot flush coming on	Lessen hot flush annoyance	Dyer et al. (2008)
Citrus sp.	Tyrosinase inhibition	In vitro tyrosinase activity inhibition	Significant activity	Lante and Tinello (2015)
Citrus sinensis	Antimicrobial	*B. subtilis*, *C. albicans*, *E. faecalis*, *E. coli*, *S. aureus*	No activity	Acheampong et al. (2015)
Citrus aurantifolia	Antimicrobial	*B. subtilis*, *C. albicans*, *E. faecalis*, *E. coli*, *S. aureus*	Good activity	Acheampong et al. (2015)
Citrus aurantium	Antimicrobial	*A. sydowii*, *C. sphaerospermum*, *P. chrysogenum*	Strong activity	Vito et al. (2017)
Citrus aurantium	Antimicrobial	*S. aureus*, *L. monocytogenes*, *B. cereus*, *E. coli*, *S. typhimurium*	No activity	Degirmenci and Erkurt (2020)
Citrus limon	Antimicrobial	*E. coli*, total microbial counts	Significant activity	Irkin et al. (2021)
Citrus hystrix	Antimicrobial	*F. oxysporum* f. sp. *cubense*	Significant activity	Paramalingam et al. (2021)
Citrus aurantium	Antioxidant	FRAP	Weak activity	Kalemba-Drozdz and Cierniak (2019)
Citrus aurantium	Antioxidant	DPPH, •OH scavenging assay	Good activity	Degirmenci and Erkurt (2020)

used for medicinal purposes for treating rheumatic disorders and as a gastric stimulant (Fernandez-Andrade et al. 2016). Insecticidal and nematocidal activities of bay laurel are also reported, which makes it suitable for application in organic farming system (Chahal et al. 2017). Bay laurel essential oil contains 1,8-cineol and eugenol as main compounds (Ordoudi et al. 2022), while the main compound in all studied bay laurel hydrolates was 1,8-cineole (from 39.5% to 69.2%) (Table 17.19).

Biological activities of bay laurel hydrolates according to literature is given in Table 17.20. The antimicrobial activity in a model food system shows that bay laurel is successful in reducing the microbiological contamination in fresh cut fruits and vegetables (Tornuk et al. 2011, 2014). Concentrated hydrolates shown significant antimicrobial activity, while non-concentrated hydrolates significantly reduced biofilm formation (Šilha et al. 2020). Furthermore, low antimicrobial and antioxidant activities are also reported (Ovidi et al. 2021).

Table 17.19 *Laurus nobilis* chemical composition of recovery essential oil from hydrolate

Plant material	Recovery oil	Reference
Laurus nobilis	1,8-Cineole (39.5%), methyl eugenol (17.5%), α-terpineol (13.0%), eugenol (10.0%)	Di Leo Lira et al. (2009)
Laurus nobilis	1,8-Cineole (69.2%), α-terpineol (10.6%)	Di Leo Lira et al. (2009)
Laurus nobilis	1,8-Cineole (58.7%)	Paolini et al. (2008)
Laurus nobilis	1,8-Cineole (56.4%), terpinene-4-ol (6.0%), α-terpineol (5.0%)	Šilha et al. (2020)
Laurus nobilis	1,8-Cineole (65.1%), α-thujone (11.1%), camphor (9.1%), borneol (8.4%)	Ovidi et al. (2021)

Table 17.20 Biological activity of *Laurus nobilis* hydrolates

Plant material	Activity	Method	Result	Reference
Laurus nobilis	Antimicrobial	*E. coli* and *S. typhimurium*	Significant activity	Tornuk et al. (2011)
Laurus nobilis	Antimicrobial	*S. aureus*	Significant activity	Tornuk et al. (2014)
Laurus nobilis	Antimicrobial	*A. butzleri*, *A. cryaerophilus*, *A. lanthieri*, *A. skirrowii*, *A. thereius*, *S. aureus*, *E. faecalis*, *P. aeruginosa*, *E. coli*, *C. albicans*	Significant activity	Šilha et al. (2020)
Laurus nobilis	Antimicrobial	*E. coli*, *P. fluorescens*, *A. bohemicus*, *B. cereus*, *K. marina*	No activity	Ovidi et al. (2021)
Laurus nobilis	Antioxidant	DPPH, ABTS	Low activity	Ovidi et al. (2021)

17.13 Conclusion

Lavender, thyme, oregano, savory, mint, sage, rosemary, rose, citrus, and bay laurel are species widely used for essential oil extraction. During this process, hydrolates are obtained as by-products. This review gathers scientific evidence about research carried out on their chemical characterization and biological activity. Primary decanted essential oil has similar chemical composition to the selected hydrolate and the recovery essential oil from the hydrolate. Their hydrolates are potential active antimicrobial and antioxidant raw material. However, the valorization of these by-products is mandatory, for obtaining additional profit, as well as from the aspect of environmental protection, to reduce waste material of medicinal plant processing,

as well as to reduce application of synthetic preservatives in food industry or synthetic pesticides in agriculture. Hydrolates are highly valued in aromatherapy because they can be applied undiluted without health risks and in cosmetic industry (as replacement for the water phase). Further prospects in the research of hydrolates needs to be in the development of technology, i.e., preparation based on hydrolates for industrial application. Currently, this is the case only with rose hydrolate which is used for redistillation, i.e., obtaining secondary oil which is mixed with primary oil for obtaining the final product.

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Chapter 18
From Agricultural Waste to Functional Food Products: An Overview

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Abstract Scientific research in the field of food provides a lot of evidence that supports the view that diet is the main variable determinant of chronic diseases. Although the concept of the positive impact of diet on human health dates back to the fifth-century BC when Hippocrates said, '*Let food be your medicine and medicine your food*', modern consumers demand it due to the fact that food has changed significantly over the last decades. According to the World Health Organization (WHO), 71% of deaths are caused by new-age diseases, such as obesity, diabetes, cancer and cardiovascular and respiratory diseases annually. It is estimated that 80% of these diseases can be avoided by changing the diet, which has led to an increase in consumer health awareness in the direction of interest in food that contributes to a healthier lifestyle. However, the modern way of life imposes food that is quick and easy to prepare and which most often, in addition to meeting basic nutritional and energy needs, does not improve health and physical fitness. For these reasons, the production of functional food, as food with health-improving effects, has extraordinary potential and is the foundation of the development of the modern food industry around the world. On the other hand, the expansion of the food industry leads to the creation of a large amount of biowaste material or a specific by-product with a high content of bioactive compounds. Generating these types of by-products represents a significant environmental problem and economic deficit. Consequently, their valorization into economically viable food products is supported by the concept of a circular bioeconomy, and one of the ways is the production of functional ingredients intended for the food industry. Therefore, this chapter offers a review of the scientific-relevant literature that deals with obtaining bioactive compounds from plant-based agriculture waste and their addition to the food in order to create different types of functional food products.

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18.1 Introduction

The agricultural and food industries are the leading industries in the world, with a long tradition and great importance for the entire economy of a large number of countries. However, the development of these industries leads to the creation of a large amount of waste material or specific by-products, which utilization represents imperative from a social, environmental and economic point of view (Lin et al. 2009). According to the definition of the European Parliament Directive, agricultural and food waste can be a biodegradable material (biowaste) that is subject to anaerobic and aerobic fermentation processes (Directive 2008/98/EC 2008). Disposal of this type of waste is a significant environmental problem, as they are subject to microbiological degradation and autooxidation due to high water content and active enzymes and consequently uncontrolled oxygen consumption and greenhouse gas emissions (Ndubuisi Ezejiofor et al. 2014). On the other hand, this problem is also characterized by an economic deficit, where in addition to food and agricultural inputs, resources such as energy and water are lost during food production (Galanakis 2012). Based on the Food and Agriculture Organization (FAO) data, one-third of the world's food production lags or is not used, amounting to about 1.3 billion tons annually. Within the European Union (EU), the same problem reaches a value of 90 million tons annually, of which 39% comes from the food industry. According to the legal regulations of the EU, these substances have the status of waste, but the term 'by-product' is used in the food industry and can be of plant or animal origin:

1. Fruits and vegetables: pulp, peel, stalks, skin and seeds
2. Tuberous vegetables: potato peel, discarded potatoes, potato juice and potato chips
3. Oilseeds and legumes: husks, parts of the grain and meal and bread (sunflower, soybean)
4. Cereals: husks, sprouts, bran, fodder flour and corn gluten
5. Sugar beet: leaves, sugar beet noodles, sugarcane pulp and molasses
6. By-products of the wine industry: grape pomace, wine lees, grape seed and stalks
7. By-products of the beer industry: malt germ, brewer's beer and brewer's yeast
8. By-products of the meat-processing industry: leather, blood, hair, horns, bones, etc.
9. Fish and seafood: bones, heads, caviar, offal, shell and scales
10. Milk: whey
11. Eggs: shell (Maslovarić 2017)

According to FAO estimates (2011), the world's population will reach 9.1 billion by 2050, making an increase in the volume of food waste inevitably. Furthermore,

the additional problem can be the fact that the production of agri-food products also increased by 60% compared to the average of the previous 10 years (FAO 2011). This includes various aspects of production, processing, distribution and retail and ends with household consumption. The amount of food lost along the food supply chain in some products reaches up to 46% (Caldeira et al. 2019). Also, a disquieting fact is that the total losses of underdeveloped and developing countries are almost equal to the losses of developed countries, due to climatic conditions, inadequate equipment, unsatisfactory sanitation, logistics and infrastructure and levels of education and lack of awareness of opportunities for use (FAO 2011). It has been noticed that in developed countries, over 40% of the losses occurs in the final phase, i.e., during sales and consumption. On the other hand, in underdeveloped and developing countries, most food is lost in the initial and middle stages of the food supply chain, in the so-called post-harvest phase and during processing (Gustavsson et al. 2011).

Prevention of this environmental and socio-economic problem should be approached in different ways. For example, in developed countries, it is necessary to raise awareness of the impact of food waste on all aspects of society and thus change consumer habits. Problem-solving in underdeveloped countries is based on investing in production technology, infrastructure, storage and processing capacities, as well as in educating all actors in the food supply chain. In recent decades, experts of various profiles have been working on solving the global problem of agricultural and food waste, where the utilization of biowaste using modern technologies resulting from scientific research is one of the most important and promising approaches.

18.2 Concept of Circular Bioeconomy in Functional Food Creation Based on Agricultural Waste Compounds

From the beginning of the industrial revolution until recently, most of the generated waste has been considered and treated as useless. Nevertheless, the importance of the environmental impact, on the one hand, and the potential to be used as a source of high-added value compounds or as raw material in other industrial processes, on the other hand, has been emphasized in the last decades. This has implicated the base of a *circular economy*. It is a generic term for an industrial economy that is producing no waste and pollution, by design or intention, and in which material flows are of two types: *biological nutrients* designed to reenter the biosphere safely and *technical nutrients* designed to circulate at high quality in the production system without entering the biosphere as well as being restorative and regenerative by design.

A circular economy is opposed to a linear economy which operates on the 'take-make-dispose' model of production. It assumes that industries should work like organisms, processing nutrients that can be fed back into the cycle—whether biological or technical. The concept was presented in 1996 by Kenneth

E. Boulding in the paper entitled 'The Economics of the Coming Spaceship Earth'. Circular economy was recognized in China as a subject matter of national importance, included in China's 11th five-year plan in 2006, and has provided technical support to the practice of circular economy (NDRC 2006).

Founding principles of a circular economy include the following objectives:

1. Waste is food.
2. Diversity is strength.
3. Energy must come from renewable sources.
4. Systems thinking.
5. Prices or other feedback mechanisms should reflect real costs.

One of the most important aims of a circular economy is to raise awareness of the environmental problems already caused by our 'throwaway culture'. Regulations in environmental protection, driven by growing interest in circular economy and economic welfare, have forced the food industry to reassess the fate of by-products and side streams. Nonetheless, these waste categories are often rich in valuable compounds such as vitamins, minerals, polysaccharides, lipids, proteins, pigments, etc. (Klitkou et al. 2019). Among other trends in the modern food industry, significant effort is employed in discovering functional ingredients for the food category called 'functional food'. General economic progress, especially in Western countries, caused the worldwide rise in health awareness and interest in the quality of food we eat. In this view, the food itself has 'evolved', contributing to so-called functional nutritionism, which refers to the increased engineering and reengineering of food in coevolution with changing corporate strategies, trends in food, diets and health and new food and nutrition policies (Scrinis 2013, 2016; Vik and Kvam 2017). Among many health beneficial compounds as potential ingredients of interest for functional food formulation, antioxidants have attracted the highest interest and popularity. Recently, the rapid growth of global markets for alternative sources of proteins has also emerged the need for employing plant processing industries' by-products in producing high-quality plant-based proteins.

The circular economy in the food industry is based on the valorization of waste, changing markets, technologies and institutions through innovation. Valorization pathways are diverse, depending on the source, resources and the end-user (Turnheim et al. 2015), with the general idea of making a profit by exploiting waste. Additionally, it is necessary to be highlighted that the definition of by-products in the food industry is uncoordinated. Jasch (2009) reported that by-products are created during the production process of the main product and are not the primary goal of production, while Galanakis (2012) defines by-products as substrates separated from the food production process where functional components can be used, thus facilitating the development of new high-quality food products on the market (Rajković et al. 2020).

Besides nutrients and bioactive ingredients in functional food, by-products from food processing side streams, managed adequately, can be used as bioabsorbents, additives, animal food, microorganism growth substrate, fertilizer materials after composting or as energy sources, substrates for biofuel production, etc.

Fig. 18.1 Scheme of food industry waste management and potential valorization of valuable compounds in the food industry

(Domínguez-Perles et al. 2018; Kosseva 2011; Ghaly et al. 2013). Value-added products created from waste in the food industry primarily include animal food, food additives, prebiotics, food supplements, etc. Recovered ingredients from by-products include bioactive compounds such as phenolics, carotenoids, alkaloids, essential oils, glucosinolates and saponins, as well as nutrients such as carbohydrates, proteins, dietary fibres, oils, etc. (Fig. 18.1).

In the past decades, research on this topic has been accelerated producing data on high-value compound composition in waste and by-products as well as the possibilities for their recovery and exploitation. However, industrial solutions are still scarce. In order to close the circle, the commercialization of the recovered high-value compounds is the next step which is largely hindered. The reasons could be due to the issues during *scale-up* processes which have to be carried out in a way that functional properties of high-value compounds are preserved in the market-destined product that meets consumers' high-quality organoleptic standards. Additionally, agricultural waste collection requires additional transportation (solved by proper

management of collection process) and control of microbial growth (solved by cooling/freezing of the material and/or addition of chemical preservatives); they are produced seasonally, varying in quantity and content, and there is a high level of variation of target and non-target compounds from source to source (solved by adding a modification pretreatment step). Finally, a commercial application should be protected by IP rights, with approved health claims, which means authors have to be informed on procedures, filing rules, costs, expected revenues, etc. (Galanakis et al. 2022).

Currently, agro-industrial waste and by-products come mainly from industries' processing agricultural raw materials such as fruits and vegetables. These are rich in sugars, minerals and proteins, as well as bioactive compounds, which makes them suitable raw materials for other industrial processes. Most of them are used as animal feed or burned, anaerobically digested for producing electrical and thermal energy, and composting is widespread in the EU. In order to process agricultural by-products into valuable nutraceuticals, the following steps have to be foreseen:

1. Macroscopic pretreatment
2. Macro- and micro-molecule separation
3. Extraction
4. Purification
5. Nutraceutical formation (Galanakis 2012)

Despite the omnipresence of related studies and patented methodologies, the market existing products derived from food wastes are today rather limited, especially looking at functional food products based on agricultural waste bioactive. Current research is focused mainly on extraction and analytics, while applied researches are still not scientifically enough represented, especially in the domain of functional food formulation and related health claims. The implementation of the concept of functional food in practice is a complex and expensive procedure, preceded by clinical studies on the safety and efficacy of products in order to obtain health statements that are supporting documentation for this type of food. The outcome of this concept is the achievement of recognition and acceptability by consumers, and the field of functional food is a challenge for the scientific community, legislative practice, food and pharmaceutical industry. In terms of the perspective of production and development of new functional products, the twenty-first century is considered a century of revolution in this field. The functional food market is constantly growing, and new products are gaining increasing demand and consumer acceptance (Hasler 2002). It is important to note that the success of this revolution also lies in education. The development of information technology and numerous journals dealing with nutrition has made it possible to access a large amount of data and raise awareness of the importance of food and its impact on health (Bornkessel et al. 2014; Alexander et al. 2015).

18.3 Valorization of Plant-Based Agricultural Waste

The European Union's approach to biowaste management is based on the 'waste hierarchy', which sets priorities in waste management policy, as well as priorities in waste management at the operational level (Directive 2008/98/EC on waste). At the very top of this hierarchy is the minimization or prevention of waste generation, followed by reuse, recycling, utilization in human and animal nutrition, composting, energy recovery from waste, waste handling, waste transformation or destruction, waste placement, storage and landfilling (Monspart-Senyi 2012). Landfilling is the least acceptable solution, not only from an environmental point of view but also from an economic point of view and the costs required by this method of waste disposal (Frewer and Gremmen 2007). In recent years, there has been an increasing number of scientific literature and studies related to by-products of the agricultural industry, testing of new methods and ways of their use. The valorization of these by-products as a source of high-value compounds is becoming increasingly important, which is also a potential solution for the preservation of the environment and natural resources. By-products of industrial processing of fruits and vegetables, such as grape pomace, citrus pulp, apple trop, carrot peel and pulp, tomato waste and beet waste, are a rich source of dietary fibre and polyphenolic compounds and lag in that part of the plant material which, after processing, treated as biowaste (O'Shea et al. 2012). Proven functional properties and richness of bioactive compounds are the main features of by-products of industrial processing of fruits and vegetables, which indicates the multiple benefits of their valorization. For example, many products created in this way are a rich source of natural pigments, carotenoids, betalains or anthocyanins. These pigments can be used as a substitute for synthetic food dyes, contributing to the development of natural and quality products, with a positive effect on health. The possibility of using by-products of fruit and vegetable processing is especially important due to the low price of raw materials and also the potential production of new functional products, which are, as already mentioned, a trend in the modern food industry. As the industrial approach often does not coincide with the scientific one, the food industry does not engage in the issue of using and processing by-products without developed methodologies and uniformity of raw material quality (Kalušević 2016). Manipulation of food by-products is complicated by several aspects, from microbiological, due to inadequate biological stability and risk of contamination, to practical, where high water content has a significant impact on transport costs. Also, by-products from foods high in fat and oil are subject to autooxidation, which further causes them to spoil (Russ and Meyer-Pittroff 2004).

18.3.1 Fruit Waste

Fruit processing aims to transform fresh fruits into preserved food products. Because of ecological and environmental demands, fruit processing should minimize the amount of waste, decrease energy utilization and produce high-quality products without polluting the environment (Barta et al. 1997). The choice of fruit processing technology is very important. It is recommended to use waste-free or low-waste technologies. Waste-free technologies are created to use small amounts of water and air. Also, the closed cycle design, where there is no contaminating waste formation during production, is formed. This kind of technique is starting to spread not only in the fruit processing industry but also in the other agricultural areas, where by-products and waste can be utilized in a closed cycle. The total costs of this technology are high but still cheaper than the traditional ones. With increasing raw material and energy prices, waste-free technologies will be improved and possibly more often used. Furthermore, using new scientific and technological methods, it is possible to convert environmentally polluting waste into by-products of economic value. Several factors, like nature and quality of raw material, technological process, novelty and condition of machines and human factors, influence the utility of raw materials.

In the valorization of plant-based materials, the term *biomass* refers to organisms like microorganisms, plants and animals (living or recently dead) and different biological products, wastes and by-products (Hammond et al. 1996). Biomass waste from the fruit industry also could be found used in animal feed. During fruit processing, solid (peel, seeds, stones, etc.) and liquid waste (juices and wash water) are produced (Noguchi and Tanaka 2004; Negi et al. 2003; Gil et al. 2000), while their storage in non-appropriate conditions could bring flies and different insects or animals in processing areas. Additionally, the microbiological quality of fruit biowaste is important, and variable characteristic and obtained products should be processed immediately after being available. Often waste materials contain mouldy fruit, insects, leaves, stems, soils, etc. and should be carefully handled because they could contaminate future products (Monspart-Senyi 2012).

Fruit waste could be candied, for example, peels from oranges or lemons could be used in some snacks or baked products. Mango, apricot and peach seeds contain oils or fat. Grape or papaya seeds contain oils and are appropriate for a particular group of consumers. Citrus peel oil, produced by cold pressing procedure, could achieve a very good price on the market. Apple or citrus waste could be used for pectin production. Pectin is often used as a gelling agent used in marmalades, jams and some jelly products or pharmaceutical or medical products. In some cases, fruit pulp could be transformed into fruit pieces, but the process is relatively complicated, and there is a low demand for these products. For example, enzymes from some fruits could be harvested (papain from papaya, bromelain from pineapple or ficin from figs). Citrus enzymes could convert cellulose to sugar, for fermentation processes. Often these procedures are not economically reasonable. Banana stems could be used for growing food yeasts or could be candied and sweets could be produced.

Sometimes, wine or vinegar could be used from fruit (most often grape) waste. Also, fibres or natural colours could be obtained from different fruit wastes. Madhuri and Kamini-Devi (2003) published the potential use of watermelon peel for products such as pickles, tutti-frutti, vadiyams or cheese. Hammond et al. (1996) conducted a study where banana waste was potentially used to obtain ethanol. Bioactive compounds present in fruit or vegetable processing waste could be extracted and added to different food products, like carotenoids from carrot waste in pasta (Šeregelj et al. 2022) and anthocyanins from sour cherry pomace in cookies (Tumbas Šaponjac et al. 2016). Flavonoids present in mandarins possess fungistatic activity (Chkhikvishvili and Gogiya 1995), while Manthey and Grohmann (2001) found out that limonoids present in citrus fruit, and also in lemon waste, have good pharmacological properties and could be used as insect antifeedant in agriculture. Water vapour permeability insignificantly increased, when gelatin films were enriched with pomegranate peel powder. Hydrophobic and hydrophilic compounds in the peel of pomegranate balance the hygroscopic characteristics and do not alter the moisture content of the films (Hannani et al. 2019).

18.3.2 Vegetable Waste

Same as in the fruit processing industry, the vegetable industry should reduce amounts of waste, recycle present valuable substances and upgrade processing technologies. After vegetable processing, waste bioactive compounds and health beneficial compounds remain at the same level as in fruits. Besides all the problems, a big problem is the formation of off-odours, which are very unpleasant (Tagesschau 1999). There are some limits on the usage of vegetable waste. According to Laufenberg et al. (1996), protein concentrate made of potato waste could only be used by cattle due to the high potassium content. The olive cake is not recommended for feeding because of its low digestibility (Clemente et al. 1997). Sugarcane bagasse contains high levels of lignin, which interact with cellulose, causing low digestibility for animal food usage (Purchase 1995).

There are still plenty of possible usages of vegetable waste. Vegetable waste is often raw and added to bread, pies, cookies, jams, cakes, etc. Sometimes bioactive compounds present in vegetable waste are encapsulated in some matrix and then added to food products. Carrot (Šeregelj et al. 2022) or beet-root (Hidalgo et al. 2018) waste added to food could stabilize the natural colours and improve the vitamin and fibre content, making value-added products. Also, Šeregelj et al. (2019) used phenolics and carotenoids from red peer waste for obtaining functional yogurt. Urrestarazu et al. (2005) published a study where almond shells could be used as ecologically friendly growing media. Virgin vegetable oil or waste cooking oil could be used for the production of biodiesel (Zhang et al. 2003). Possible usage of waste frying, sunflower or non-edible vegetable oil, as an alternative fuel for a diesel engine, was published by Pugazhvadivu and Jeyachandran (2005). Potato peel

showed good properties and possibilities in biodegradable food packaging (Borah et al. 2017).

18.3.3 Others

Besides fruit and vegetable waste, for example, shells from seafood or fish waste could find usage. Sachindra and Mahendrakar (2005) published a study where valuable bioactive compounds, carotenoids, were extracted from shrimp waste. Shrimp waste is known as a rich source of astaxanthin, where refined sunflower oil gave the highest carotenoid yield compared to other vegetable oils studied (Sachindra et al. 2006). Fish waste has become an issue of public concern. Because of this, treated fish waste could have many possible usages: animal feed, biodiesel/biogas, dietetic products (chitosan), natural pigments, food packaging applications (chitosan), cosmetics (collagen), enzyme isolation, soil fertilizer and moisture control in foods (Arvanitoyannis and Kassaveti 2008). Fish gelatin, as fish waste, is known as a valuable biopolymer for biofilms because of its biodegradable nature and high myofibrillar protein content (Etxabide et al. 2017). The addition of pomegranate peel powder in gelatin films significantly increased their water vapour permeability (Hannani et al. 2019). Components present in the peel of pomegranate balance the hygroscopic properties and do not change the moisture content of the films. Different peels were added in fish gelatin/polyethylene bilayer films. Their solubility was lowered in these cases (Etxabide et al. 2017).

18.4 Agricultural Waste Bioactive Compounds as a Functional Food Ingredient

Population growth and rapid urbanization have led to an increased demand for processed foods. In this regard, the food industry experiences accelerated development to meet the requirements of numerous consumers. For example, agricultural industries usually generate a large amount of organic waste, including the waste from the maintenance of farms and crops (agricultural waste) and the industrialization of the product (food industry waste) (Leyva-López et al. 2020). Such an amount of waste represents a significant environmental and public health issue. On the other hand, agricultural waste is a commonly rich source of bioactive compounds and nutrients. According to the available literature data, some fruit and vegetable non-edible parts, such as peels, skin, seeds and twigs, often contain significantly higher amounts of bioactive compounds when compared to the edible parts (Othman et al. 2020). For example, sweet potato peels are reported to have more than 50% higher content of phenolic compounds than edible parts (tuber) (Šeregelj et al. 2020). It is also noted that peels of apple, citrus fruits, grapes and seeds of mango and

avocado have more than 15% higher phenolic content than pulp (Othman et al. 2020). Generally, these recovered biomolecules can serve as natural antioxidants for the formulation of functional foods or as additives in food products to extend their shelf life (Kalogeropoulos et al. 2012).

Several plant-based wastes can be used to obtain bioactive compounds. The main compounds found in agricultural wastes with defined biological and technological properties and great interest in food applications are presented in Fig. 18.1. Additionally, Table 18.1 summarized some of the important agricultural wastes and valorized bioactive compounds, especially those of the most consumed fruits and vegetables in the human diet.

18.4.1 Bioactive Compounds in Agricultural Waste for Food Applications and Health Benefits

The trend for foods with beneficial effects on health, while contributing to the sustainable use of natural resources, is supported by a large number of studies that report the addition of bioactive compounds from agricultural waste in various food matrices. Bioactive compounds can be used for different reasons: (1) to improve conventional food quality, i.e., their nutritional, sensory and technological properties, (2) to produce functional foods that provide physiological and nutritional benefits and (3) to produce additives, isolated components of food or agricultural wastes that provide proven health benefits (Lemes et al. 2022). This wide application of bioactive compounds occurs due to several health benefits attributed to bioactive compounds (Fig. 18.2), including protection of the immune system, anti-inflammatory action, reduction of damage from cell oxidation, the occurrence of chronic non-communicable diseases and ability of intestinal microbiota modulation (Silva et al. 2019; Alongi and Anese 2021).

When bioactive compounds are mentioned, the first thing that comes to mind is their antioxidant activity. Namely, free radicals, reactive oxidative and nitrogen species are normally generated in our bodies driven by multiple endogenous reactions and states. Those free radicals appear in many shapes, sizes and configurations. What they share is the need for electrons, which they find in nearby substances. In such a way, free radicals make progressive damage to the main structure of our body. For example, free radicals can influence the change in the instructions coded in DNA or disrupt the substance's flow through the cell membrane. In the progressive stadium, when the amount of free radicals is critically high, it can cause a condition called oxidative stress that can lead to many chronic diseases. Therefore, antioxidants are substances mainly present in food that are capable of neutralizing or reducing the damage caused by free radicals (Leyva-López et al. 2020). Taking into account that agricultural waste is a rich source of bioactive compounds, obtaining those compounds by extraction and purification can be a first step before their application in the food industry gaining the products with added value. For

Table 18.1 Bioactive compounds in different plant-based agricultural waste residues

Fruit/ vegetable	Type of waste	Class of bioactive compounds	Major compounds	Reference
Apple	Pomace	Phenolic acids	Chlorogenic, caffeic, ferulic, *p*-coumaric, sinapic and *p*-coumaroylquinic acids	Barreira et al. (2019), Lavelli and Corti (2011), Ćetković et al. (2008)
		Flavonoids	Rutin, isorhamnetin, kaempferol, quercetin, rhamnetin, glycoconjugates, hyperin, procyanidin B_2, (+)-catechin and (−)-epicatechin	
		Anthocyanins	Cyanidin-3-*O*-galactoside	
		Di-hydrochalcones	Phlorizin and phloretin	
Apricot	Pomace	Phenolic acid	3-caffeoylquinic, 5-caffeoylquinic and chlorogenic acids	Dulf et al. (2016), Cheaib et al. (2018), Kasapoglu et al. (2020)
		Flavonoids	Quercetin-3-rutinoside, quercetin 3-O-(6″-acetyl-glucoside), catechin and epicatechin rutin	
		Carotenoids	α-, β- and γ-carotene	
Banana	Peel	Phenolic acids	Ferulic, cinnamic, alpha-hydroxycinnamic, sinapic, *p*-coumaric and caffeic acids	Tallapally et al. (2020), Behiry et al. (2019), Avram et al. (2022), Vu et al. (2018)
		Flavonoids	Kaempferol, quercetin, isoquercitrin, rutin, myricetin, naringenin, laricitrin, catechin, epicatechin and gallocatechin	
		Catecholamines	Dopamine and L-dopa	
Beetroot	Pomace	Phenolic acids	Ferulic, vanillic, *p*-hydroxybenzoic, caffeic, protocatechuic and *p*-hydroxybenzoic acids	Vulić et al. (2014)
		Flavonoids	Rutin, catechin and epicatechin	
		Betalains	Betacyanins (betanin and isobetanin) and betaxanthins (vulgaxanthin I)	
Berries from	Berries press residue	Phenolic acids	Chlorogenic, caffeic and 4-hydroxcinnamic acids and procyanidins B_1 and B_2	Lončarić et al. (2020), Klavins et al. (2018)

(continued)

Table 18.1 (continued)

Fruit/ vegetable	Type of waste	Class of bioactive compounds	Major compounds	Reference
Vaccinum genus		Flavonoids	Catechin, epicatechin, myricetin, quercetin and kaempferol	
		Anthocyanins	Glycoconjugates of delphinidin, petunidin, cyanidin, peonidin and malvidin	
		Carotenoids	β-Carotene and β-cryptoxanthin	
Broccoli	Stalks and florets	Phenolic acids	Chlorogenic, neochlorogenic and sinapic acids	Thomas et al. (2018)
		Flavonoids	Kaempferol and quercetin	
		Glucosinolates	Glucoiberin, glucoerucin, glucoraphanin, gluconapin, glucoalyssin, glucobrassicin and neoglucobrassicin	
Carrot	Pomace	Carotenoids	α- and β-carotene and *cis*-β-carotene	Šeregelj et al. (2021)
		Tocopherols	α-, β- and γ-tocopherol	
Cabbage	Leaves waste	Flavonoids	Quercetin glycoside, kaempferol glycoside, quercetin and kaempferol	Kowalski et al. (2021)
Cauliflower	Stems and leaves	Phenolic acids	Ferulic and sinapic acids	Gonzales et al. (2014), Amofa-Diatuo et al. (2017)
		Flavonoids	Kaempferol and quercetin glycosides	
		Isothiocyanate	–[a]	
Elderberry	Branch waste	Phenolic acids	Chlorogenic acid	Silva et al. (2017)
		Flavonoids	Quercetin and its glycoconjugates	
		Anthocyanins	Cyanidin and its glycoconjugates	
Grape	Pomace	Phenolic acids	Two hydroxybenzoic acids and two hydroxycinnamic acid derivatives	Peixoto et al. (2018)
		Flavonoids	Eleven flavan-3-ols (catechin and epicatechin derivatives and proanthocyanidins) and six flavonols (quercetin, laricitrin and syringetin derivatives)	
		Anthocyanins		

(continued)

Table 18.1 (continued)

Fruit/ vegetable	Type of waste	Class of bioactive compounds	Major compounds	Reference
			Malvidin, delphinidin, petunidin and peonidin derivatives	
Mango	Kernel seed	Phenolic acids	Gallic acid and its derivatives	Torres-León et al. (2016)
		Flavonoids	Quercetin, isoquercetin, fisetin, epicatechin, epigallocatechin and epicatechin gallate	
		Hydrolysable tannins	–	
Plum	Pomace	Phenolic acids	Chlorogenic and neochlorogenic acids	Sójka et al. (2015)
		Flavonoids	Quercetin glycosides, kaempferol and rutinoside	
		Anthocyanins	Cyanidin and peonidin glycosides	
Potato	Peel	Phenolic acids	Chlorogenic and caffeic acids	Wu et al. (2012), Friedman et al. (2017)
		Glycoalkaloid	α-Chaconine and α-solanine	
Pumpkin	Peel	Phenolic acids	Protocatechuic, *p*-hydroxybenzoic, *p*-hydroxybenzaldehyde, vanillic, caffeic, syringic, trans-*p*-coumaric, ferulic and trans-sinapic acids	Salami et al. (2021)
		Carotenoids	Neoxanthin, violaxanthin, luteoxanthin, lutein, zeaxanthin, 13-cis-β-carotene, β-carotene, α-carotene, α-cryptoxanthin, 9-cis-β-carotene, β-cryptoxanthin and lycopene	
Peach	Pomace	Phenolic acids	*p*-Coumaric, *p*-hydroxybenzoic, caffeic and chlorogenic acids	Cvetković et al. (2021)
		Flavonoids	Catechin, epicatechin, rutin and quercetin	
		Carotenoids	β-Carotene and β-cryptoxanthin	

(continued)

Table 18.1 (continued)

Fruit/ vegetable	Type of waste	Class of bioactive compounds	Major compounds	Reference
Rep pepper		Phenolic acids	Gallic, vanillic, protocatechuic, sinapinic, caffeic, rosmarinic and chlorogenic acids	Šeregelj et al. (2019)
		Flavonoids	Epicatechin, rutin, quercetin and myricetin	
		Carotenoids	β-Carotene, lutein, zeaxanthin and β-cryptoxanthin	
Sweet potato (orange)	Peel	Phenolic acids	Gallic, vanillic, caffeic and coumaric acids	Šeregelj et al. (2020)
		Flavonoids	Catechin, epicatechin and rutin	
		Carotenoids	β-Carotene	
Tomato	Pomace	Phenolic acids	Gallic, ferulic and coumaric acids, phloridzin and phloretin	Palomo et al. (2019)
		Flavonoids	Procyanidin B_2, apigenin-7-*O*-glucoside, kaempferol-3-*O*-glucoside, luteolin-7-*O*-glucoside, genistein, kaempferol, daidzein, quercetin, quercitrin, rutin and epicatechin	
		Nucleosides	Adenosine, inosine and guanosine	
		Carotenoids	Lycopene and β-carotene	

[a] Data does not exist

instance, bioactive compounds such as essential oils, flavonoids, tannins, phenolic acids, carotenoids and tocopherols can be easily isolated from agro-industrial wastes and incorporated in meat by-products, bakery products, vegetable oils, cookies, etc. (Shirahigue and Ceccato-Antonini 2020; Akter and Rabeta 2021).

The big class of bioactive compounds is represented by polyphenols. Polyphenols, i.e., phenolic acids and flavonoids, have a high capacity for scavenging free radicals, thus being suitable to be used in food products as antioxidants. As can be seen from Table 18.1, polyphenols can be recovered from many fruit and vegetable wastes. Several authors reported that polyphenols recovered from apple pomace exhibit strong antioxidant activity, even stronger than vitamins C and E (Ćetković et al. 2008; Diñeiro García et al. 2009; Lavelli and Corti 2011; Barreira et al. 2019). Grape pomace is a rich source of polyphenols as well; hence, it has been used in many food products with the aim to enhance health benefits and nutritional value of

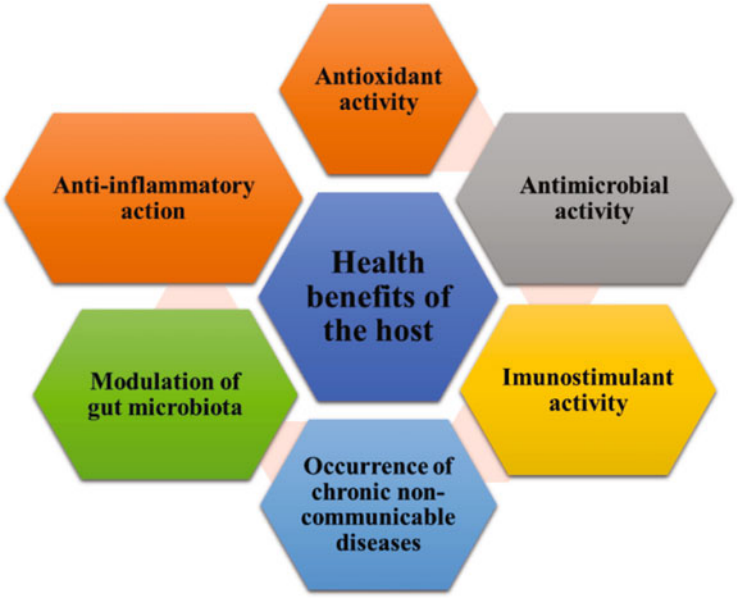

Fig. 18.2 Health benefits of bioactive compounds

the products. Furthermore, recent studies evaluated the use of polyphenol-rich extracts from agricultural waste for improving the product's shelf life by preventing discolouration and oxidative processes. For these purposes, Muino et al. (2017) evaluated the use of extract from olive oil waste to act as a natural antioxidant in lamb meat patties and noted very promising results. Farvin et al. (2012) reported that adding antioxidants from potato peel extracts in minced horse mackerel had also a positive impact on product preservation. Similar results were obtained in the study reported by Albertos et al. (2015) when polyphenolic extract from carob seed peel was used as an antioxidant in minced horse mackerel.

Other significant bioactive compounds are natural pigments, with great benefits for human health, due to their antioxidant properties, but they are also used as food colourants. Most utilized in the food industry, for their antioxidant and colouring effect, are carotenoids, anthocyanins and betalains. Some examples of products in which recovered natural pigments from waste were incorporated include pasta (Šeregelj et al. 2022), water biscuits (Hidalgo et al. 2018), refined vegetable oils (Benakmoum et al. 2008), yogurt (Šeregelj et al. 2021), etc.

In most cases, the antioxidant activity of natural products and compounds comes coupled with antimicrobial activity. Today, it is well known that, for example, fruit by-products such as peel and seed fractions have higher antimicrobial activity than the other main fractions. Numerous studies have demonstrated the presence of bioactive compounds with high antimicrobial properties in lemon peels (Mahmud et al. 2009), pomegranate peels (Al-Zoreky 2009), grape seeds (Adámez et al. 2012), mango peel and kernel and onion leaves (Nasser et al. 2014), Osage orange leaves

(Filip et al. 2020), etc. Moreover, extracts made from agro-waste (garlic, ginger, onion and potato peels) were recently tested against different pathogenic bacterial and fungal strains, i.e., *Escherichia coli*, *Bacillus megaterium*, *B. cereus*, *Staphylococcus aureus*, *Colletotrichum falcatum*, *Fusarium moniliforme* and *Rhizoctonia solani* (Naqvi et al. 2020). The results showed the remarkably antimicrobial potential of ginger peel, moderate to high activity of garlic and minimal or no activity of onion and potato peel. The gram-positive bacterium, *Staphylococcus aureus*, seems to be the most susceptible to the tested agro-waste extracts. Also, a positive inhibition zone for tested extracts, except for onion extracts, was observed against all tested fungi. Similar results of antimicrobial activity were obtained in the case of Osage orange leaf extracts (Filip et al. 2020). Also, hydrosols obtained from the distillation process of aromatic plants as a by-product are under intensive investigation for their antioxidant and antimicrobial potential (Aćimović et al. 2022). In this point of view, by-products from tee manufacturing (Pavlić et al. 2017) have been considered a carrier of bioactive compounds, as well as the essential oils of a wide spectrum of plants (Riabov et al. 2020; Micić et al. 2021). Liquid by-products such as winery effluent, also rich in bioactive compounds with considerably antimicrobial activity, are nowadays used for obtaining a health-promoting beverage called kombucha (Vukmanović et al. 2022).

Besides antioxidant and antimicrobial activity, compounds extracted from the agricultural waste may also express immunostimulant activity. Immunostimulators or immunomodulators are naturally occurring substances that have the task to adjust the immune system of the host in such a way to spawn resistance to the presence of pathogens or diseases. In order to track the immunostimulant potential of a substance, the following biomarkers are used (Leyva-López et al. 2020):

1. Tracing the enzymatic activity of lysozyme (which influences the lysis of peptidoglycans, a structural component of the gram-positive bacteria cell wall) and myeloperoxidase (which causes the formation of various acids: hypochlorous, hypobromous and hypothiocyanite acid).
2. Checking the phagocytic potential of immune cells by measuring the generation of superoxide anion by nitroblue tetrazolium reduction method.
3. Measuring the count of blood cell indicators such as red and white cells, neutrophils or hematocrit levels. By the increase or decrease in the number of targeted blood cell indicators, it can be assumed that a substance has the ability to provoke a response of the host's immune system.
4. Evaluating other immunological parameters, such as the concentration of immunoglobulins and the level of proteins.

Today, it is a trend to isolate immunostimulators from low-cost, natural sources such as agricultural waste. Up to now, there are only a few scientific papers dedicated to the utilization of agricultural waste as a source of immunostimulators that can be used for therapeutic purposes. El-Hawary and Rabeh (2014) reported on *Mangifera indica* peels' impressive immunostimulant, anticancer and antimicrobial potency. Namely, this group of researchers indicates that essential oils from mango

peels can be used as therapeutic in the treatment of many infectious diseases and for immune stimulation of patients with breast cancer.

Reaching gut microbiota homeostasis is a highly attractive topic for researchers. New insights in this area indicate that bioactive compounds such as polyphenols may contribute to gut microbiota modulation, playing a double role. More precisely, Vaíguez-Daza et al. (2021) introduce the concept of the polyphenol duplibiotic effect, acting as an antimicrobial agent for pathogenic species and growth promoter for beneficial bacteria (prebiotic effect) at the same time. Although prebiotics are usually considered as non-digestible carbohydrates, the International Scientific Association for Probiotics and Prebiotics (ISAPP) recently revised the previous definition by including the plant polyphenols as potential prebiotics (Gibson et al. 2017). By consuming polyphenol-rich food or supplements, some of the following health benefits can be expected: avoid or attenuate metabolic and inflammatory diseases, promoting host intestinal mucus production, and activate the production of immunoglobulins and gut peptides with antimicrobial effect, regulation of hepatic bile acids, etc. (Vaíguez-Daza et al. 2021). As a positive thing, plants produce over 100,000 secondary metabolites, and a part of them intend to have the ability to interact with gut microbiota. According to this, there is room for extensive research in this area.

A few plant alkaloids, berberine and betalain, have already demonstrated the ability to act as both antimicrobial and prebiotic substances (Song et al. 2016; Roriz et al. 2018). The main problem in studying polyphenols as duplibiotics is the experimental setups. In vitro studies are carried out as individual bacterial strains or simplified bacterial consortiums, but they lack direct interaction with the host. On the other hand, the formation of gut microbiota culture or testing in animal models provides a new set of information, but the experiment setup is complex and hard to achieve. In the future, well-designed and realistic human clinical studies should be crucial for unravelling the mechanism of gut microbiota utilization of polyphenols and their role in providing health benefits for the host.

18.4.2 Bioactive Compounds and Dietary Fibres in Agricultural Waste as Potential Prebiotics for Food Applications and Health Benefits

Some bioactive compounds and dietary fibres can act by stimulating the growth and metabolic activity of probiotic bacteria, especially lactic acid bacteria, while the others can be beneficial in terms of improving the nutritional and functional properties of food products (Chamorro et al. 2022). Therefore, the production of prebiotics from agricultural waste is under investigation worldwide.

According to Gibson and Roberfroid (1995), probiotics are defined as 'non-digestible food ingredients that beneficially affect the host by selectively stimulating the growth and/or activity of one or a limited number of bacteria in the colon and

thus improves the host's health'. The complete mechanism of prebiotics has long been unclear. Today, it is known that non-digestible carbohydrates pass through the upper digestive tract and hence are fermented in the colon by host microbiota. There, in the colon, microorganisms produce metabolites such as short-chain fatty acids (acetate, lactate, propionate and butyrate), influencing the decrease of pH value of the environment. The acid environment favours the proliferation of bifidobacteria and lactobacilli and at the same time reduces the chance for pathogen growth and viability (Lamsal 2012; Slavin 2013). However, not all carbohydrates can be declared as prebiotics. There are a few requirements that carbohydrates should fulfil in order to be considered prebiotic:

1. Resistance to gastric acidity, hydrolysis by any endogenous enzymes and gastrointestinal absorption
2. Consumption and fermentation by intestinal microflora
3. Selective stimulation and/or activity of health-contributing intestinal bacteria (Gibson et al. 2004)

Among oligosaccharides fructo-oligosaccharides (FOS) and galacto-oligosaccharides (GOS) and inulin are well known for their prebiotic activity and are commercially available and accepted as food-grade prebiotics. Still, in recent years, scientific attention has been directed to other high-performing and lower-cost prebiotics such as pectic oligosaccharides (POS), xylo-oligosaccharides (XOS), arabinoxylo-oligosaccharides (AXOS) and isomalto-oligosaccharides (IMOS) (Kumar Awasthi et al. 2022). All these oligosaccharides can be found in various biowastes including rice straw, husk, fruit and vegetable peel, sugarcane bagasse, spent tea leaves, corn stalk, corn stover, etc. POS is generally obtained by the depolymerization of pectin. This biopolymer can be found as a component of the primary cell wall in plants, providing cell adhesion and contributing to the textural properties of plant organs. The latest research is dedicated to the prebiotic activity of POS due to their ability to shape the gut microbiota influencing the gut homeostasis (Vazquez-Olivo et al. 2018; Zhang et al. 2018). POS extracted from different types of agricultural wastes can be cut into shorter chains using various enzymatic, chemical and physical techniques. It has been proven that the prebiotic activity of POS is strongly correlated with the molecular weights of oligosaccharides. Even when the molecular weight between oligosaccharides is similar, the differences in prebiotic activity can be noticed as a result of linkage between monosaccharide residues, the degree of esterification and methylation, etc. (Vazquez-Olivo et al. 2018).

As it can be seen in the available literature and modern studies, agro-industry waste and by-products are labelled as a rich source of POS. Namely, in the case of orange peel, a presence of arabinose, glucose and galacturonic acid as dominant oligosaccharides is noticed (Di et al. 2017). Investigation of the prebiotic potential of citrus peel demonstrated the existence of L-rhamnose, D-galacturonic acid, D-glucose and D-galactose (Zhang et al. 2018). Studies on the potential of pineapple waste as a growth medium for lactobacilli also indicate the presence of the POS in residual pulp, peels and skin after pineapple processing. Also, spent coffee grounds seem to

be a rich source of galactomannans and arabinogalactans because just a small fraction of these oligosaccharides is extracted during the beverage preparation (Sarghini et al. 2021).

Relatively uninvestigated oligosaccharides in terms of potential prebiotic activity are AXOS and IMO. AXOS are short arabinoxylans that contain a xylose backbone and one arabinose moiety. A limited number of studies indicate that the main sources of agro-industrial waste are barley flour and Brewer's spent grain (Sajib et al. 2018). The perspective of AXOS as prebiotic compounds is proved as the ability of *Lactobacillus brevis* and *Bifidobacterium adolescentis* to utilize AXOS from Brewer's spent grain (Sajib et al. 2018). IMO are composed of α-D-*O*-glucose linked by α-(1 → 6)glycosidic bonds. These oligosaccharides are usually found in corn or rice starch which is considered as a by-product (Plongbunjong et al. 2017). The same group of authors showed the great potential of IMO in promoting the proliferation of bifidobacteria and lactobacilli. Still, the mechanism of prebiotic activity of this group of oligosaccharides remains unknown.

18.5 Functional Food as a Source of Valuable Waste Compounds

18.5.1 Term 'Functional Food'

Functional food has many definitions, none of them officially approved, pointing to the fact that this area is still not regulated and harmonized. The term functional food was first used in 1988 in Japan and referred to food products enriched with components that have a beneficial effect on specific body functions (Ohama et al. 2006). In 1991, the Japanese Ministry of Health introduced a rule for approving a specific category of healthy food called Foods for Specified Health Use (FOSHU). For a food product to receive FOSHU status, it is necessary to have scientific evidence of the health or physiological effects. The importance of functional food production, seen through rising health-care costs, the desire to improve the quality of life, the development of new technologies and the economic potential of the food industry was quickly recognized by European countries and the United States (Roberfroid 2000). In most of these countries, there are no legal regulations or universal definitions of functional food, which is why functional food is a concept and not a specific group of food products (Coppens et al. 2006; Stanton et al. 2005). Several organizations have proposed definitions for this food category. According to the 1994 definition of the American Academy of Sciences (Food and Nutrition Board), the group of functional foods includes food products with potentially beneficial effects on health, including any modified food or food ingredient that can provide a health effect beyond that of traditional foods of the same species (Hasler 2002). The following year, the International Food Information Council Foundation (IFIC), by simple definition, introduced functional foods as foods that

can also provide health benefits. In order to obtain an official definition of functional food, the European Commission, through an action called Functional Food Science in Europe (FUFOSE), coordinated by the International Life Science Institute (ILSI), adopted a consensus on the concept of functional food known as 'Scientific Concepts of Functional Foods' during 1999. According to this concept, functional food is defined as follows: 'Food can be considered functional if it has satisfactorily shown a beneficial effect on one or more targeted functions in the body in addition to meeting basic nutritional needs, in a way relevant to health and general health conditions of the organism and/or reduces the risk of disease'. It was also pointed out that the amount and form of the functional product ingested must be the same as in the regular diet. This means that such a product cannot be in the form of a tablet or capsule but exclusively in the form of a conventional food product (Consensus Document 1999; Roberfroid 2000), but since 2001, FOSHU products can also be in the form of tablets or capsules (Ohama et al. 2006). Since most countries view functional food as a concept and not as a special category of food, the legal regulations related to such products are numerous and depend primarily on the type of food product. In the United States, the Federal Food and Drug Administration (FDA) regulates functional foods as conventional foods or as dietary supplements (Ellwood et al. 2010). For food to receive the status of functional food, it is necessary to be supported by a health claim or disease-specific claims authorized by the FDA, as well as a statement on the structure and function claims, which have to be true but not approved by the FDA (Miletić et al. 2008). The European Union defines food as conventional food, modified food, special purpose food and medical food (Goldberg 2012). Therefore, manufacturers in Europe can use two types of statements: nutritional and health statements. Nutritional refers to the nutritional composition of foods and energy value, while health statements refer to foods that have the ability to prevent, regulate or cure (Bragazzi et al. 2017).

18.5.2 Functional Food Products Based on Agricultural Waste Present on the Global Market

As previously emphasized, carriers of food product functionality are functional compounds that can be found in their composition, and scientific research has found that quantities present in food contribute to optimal health and reduce the risk of various diseases. Therefore, the introduction of the concept of functional food in practice is associated with the enrichment of the product or some of its components with functional compounds such as dietary fibre, polyphenols, carotenoids, fatty acids, plant sterols, prebiotics, probiotics, phytoestrogens, proteins, vitamins and minerals which can be obtained from agricultural waste. Newer directions of the development of functional products include the combination of several procedures for the introduction of functional ingredients while eliminating and/or reducing the amount of ingredients with harmful effects, thus achieving multiple beneficial effects

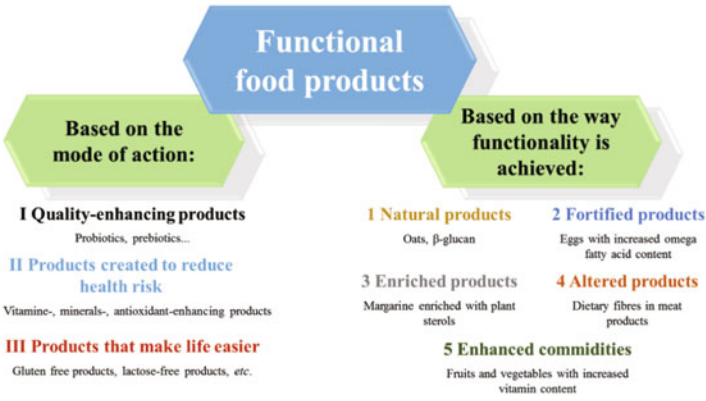

Fig. 18.3 Functional food products

on human health (Sloan 2004). In this regard, the division of functional products can be done in terms of their performance and how functionality is achieved (Fig. 18.3). The development of functional products involves three directions as follows:

1. Discovering the functional properties of traditional products
2. Finding an adequate matrix for their incorporation and design of new products
3. Determining the bioavailability of the functional component and its potential changes during product preparation (Kotilainen et al. 2006; Siro et al. 2008)

In Table 18.2, the most common functional food product representatives—yogurt (over 70% of the total functional food market) and pasta which are fortified with different compounds obtained from plant-based agricultural waste—are presented.

In the mentioned scientific-relevant research, it can be seen the trend of using by-products of the food industry as a source of functional ingredients and their potential application in the production of functional products from the group of fermented milk beverages, pasta and meat. This approach to the production of functional food products, in addition to the undoubted improvement of nutritional and health quality, provides significant progress in terms of technology, especially in terms of quality, durability and stability. Also, the pathway represented in examples in Table 18.2 is the initial step for implementation of this type of health-improving product in human daily diet and implementation of the concept presented in Sect. 18.2.

Additionally, the functional food market is very diverse and unevenly distributed in different regions of the world. As there is no legislation in most countries defining functional foods, it is quite difficult to assess the global market for these products (Kotilainen et al. 2006). However, available data indicate that North America, Europe and Japan are the three largest markets for functional foods, accounting for over 90% of total sales of functional products (Siro et al. 2008). The first estimates of the value of the global functional food market were between 33 and 61 billion dollars.

Table 18.2 Example of food products fortified with agricultural waste ingredients

Functional food product	Bioactive compounds used for fortification	Agriculture waste for extraction of bioactive compound(s)	Reference
Dairy product example			
Yogurt	Carotenoids	Carrot pomace	Šeregelj et al. (2020)
	Carotenoids and phenolic compounds	Red pepper pomace	Šeregelj et al. (2019)
	Dietary fibres	Cranberry pomace	Varnaitė et al. (2022)
		Asparagus	Sanz et al. (2008)
	Proteins and dietary fibres	Soya, pea, rice and almond	Shin et al. (2021)
	Coffee silver skin	Coffee	Bertolino et al. (2019)
	Phenolic compounds	Strawberry press residues	Ivanov and Dimitrova (2019)
		Apple peel	Ahmad et al. (2020)
		Red cactus pear peel	Hernández-Carranza et al. (2019)
		Rhubarb, grape seed, thyme, green tea and mint	Bulut et al. (2021)
	Pectin	Citrus pomace	Arioui et al. (2016)
Mill and bakery product example			
Pasta	Dietary fibres	Orange pomace	De Moraes Crizel et al. (2013)
	Phenolic compounds and dietary fibres	Tomato by-product	Padalino et al. (2017)
	Carotenoids	Carrot pomace	Šeregelj et al. (2022)
			Gull et al. (2015)
	Phenolic compounds	Apple pomace	Lončarić et al. (2014)
		Celery root and sugar beet by-products	Lucia et al. (2018)
		Artichoke canning by-products	Pasqualone et al. (2017)
		Moringa oleifera L. leafs	Simonato et al. (2020)
		Grape pomace skins	Gaita et al. (2020)
		Olive pomace	Simonato et al. (2019)

According to the statistical agency Statista, the functional food market in 2020 reached a value of 188.56 billion dollars, while an estimate of 275.77 billion dollars is projected for 2025 (Statista 2019).

18.6 Conclusions

Nowadays, agro-waste and by-products are considered a nutritional and functional raw material that can be incorporated in food or pharmaceutical formulations, obtaining the products with the additional value. Taking this into account, the reused bioactive materials from agricultural waste may be a promising solution for economic, social and environmental problems occurring because of generating the large amount of waste all around the world. Some type of agricultural waste may be directly incorporated in food formulations or as a source of proteins, lipids, vitamins, antioxidants, etc. The other components can be extracted from the waste material and further used as nutritional and functional ingredients. Moreover, prebiotics, from the agro-waste material in combination with the antioxidants, are often associated with the possible therapeutic applications in formulas that enhance the human health by improving the intestinal environment and metabolic processes with insignificant side effects. Certainly, more detailed studies in this area are mandatory in order to achieve high quality of newly designed formulations and consumer acceptance. Thus, the governments should support installing the technology of agro-waste and by-product valorization and utilization, so the achievements come fast coupled with the solving of the important environmental problems and economic growth.

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Part IV
Recent Advancements, Energy and Nanomaterials from Agricultural Waste

Chapter 19
Recent Advancements in Agricultural Residue Valorisation into Bio-Products

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Abstract Traditional and local agriculture relied on circular sustainability models; however, contemporary agriculture presently generates tonnes of garbage that are piled up in landfills and have unfavourable effects rather than being reintroduced into the production chain for a future use. However, these agricultural waste products are a rich source of bioactive substances. One of the main goals of both industrialised and developing nations is waste recycling. The biorefineries stand out as the most ideal business platform to create the essential chemical changes in relation to lignin valorisation and the circular economy. Further, the generation of

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effective products from such wastes has led to the development of novel technologies. Nanobiotechnology is an important and modern tool to valorise the agricultural residues by using nanoparticles to produce a value-added product. Also, nanomaterials can be generated using agro residues (cellulose nanocrystals (CNCs), rice husk-derived Si nanomaterials). This chapter discusses the potential sources of biomass for valorisation into different bio-commodities ranging from fuel to biopolymer application. Also, this chapter deals with the advancements in the valorisation process in terms of nanotechnology along with the challenges and future prospects.

Keywords Lignocellulose · Nanobiotechnology · Biorefinery · Bio-commodities · Recycling

19.1 Introduction

The global population is predicted to escalate from the current population scenario of 7.7–8.6 billion in 2030 and 9.7 billion by 2050 as per the report of United Nation (UN) and the Food and Agriculture Organization (FAO) (UN 2019). This states that the current system of food, shelter, water and energy will be insufficient to fulfil the demands of the growing population. This demand will produce the unavoidable impact on the surrounding niche of animal and the complete environment system. This will also interfere with the climate system and the resource production. The agriculture and food waste generation, pollution level and the resource depletion rate will also increase with the growing population. According to the present scenario, approximately 815 million children are malnourished, and the number is expected to include another two billion in the group. According to the United Nations Environmental Programme Food Waste Index report (UNEP 2021), approximately 931 million tons of food waste was generated each year from households, food service industry and retail establishers. The key finding of this programme also summarised that household per capita food waste generation is mostly analogous throughout country income groups, explaining that the food waste generation is likewise pertinent in higher, upper-middle as well as lower-middle income countries. This situation demands to revolutionise the current conventional method of safeguarding food security in a much more sustainable manner. The conventional agriculture system utilizing the chemical and being inefficient to meet the demand presents a big question of mitigation in front of researchers and agriculturalists. Waste production and its proper management is also one of the pertinent issues all over the globe. The nanotechnology and nanoscience can provide an answer to this problem to increase sustainability of the agriculture and food system.

As per Organisation for Economic Co-operation and Development (OECD), agricultural waste is referred as “waste created by the various agricultural processes comprising pesticides and fertilisers entering water system; from field, manure and other wastes from farm lands, slaughterhouses and poultry; harvest waste; that enter into water, air or soils; and salt and silt drained from fields” (Bruce et al. 2005). A

significant amount of agricultural and food production is mislaid as waste and residue.

The distinctive physicochemical features of nanomaterials like high surface area, catalytic activity, shape and size provide a roadway for developing new paradigm in agriculture. It helps in increasing the efficiency of the resource utilisation and better utilisation of the waste produced. Thus, the advance techniques and methods can help in utilisation and valorisation of agricultural residues and waste contributing to strengthen the circular economy. Nanotechnology utilises nanoparticles (NPs) as nanocatalyst that plays a substantial role in the breakdown of the lignocellulosic biomass (Hutchison 2016). The nanosize catalyst fastens the entry into the cell wall of plant and facilitates the interaction of the holocellulose releasing fermented sugar. It also improves the molecular and chemical feature of the biomass, increasing the market value (Arora et al. 2020).

Indeed, several concerns about the application aspect of utilisation of nanomaterial in agriculture are to be addressed. This chapter aims to provide an insight on how the nanomaterial can help in valorisation of agricultural residues and waste in order to give a complete new direction to the product processing and formation. The techno-economic analysis and recent advancement in the nanobiotechnology for biomass valorisation have been included in this chapter. The current challenges to reduce the research gap and recommendation to improve the residue mitigation using nanoscale material are also highlighted in the further portion of the chapter.

19.2 Chemical Composition of Various Agricultural Residues

Agriculture and food waste are one of the potent sources of carbohydrate, lipids, proteins and some phytochemicals due to the presence of dietary fibres, oils, polysaccharides, carotenoids, phenolics, vitamins and other pigments. Thus, these wastes have potential health benefits. Agricultural residue comes under lignocellulosic biomass feedstock category, that is, a carbon neutral renewable feedstock that does not affect with feeds and food stocks and is inedible. Lignocellulose biomass contains certain percentage of cellulose hemicelluloses, lignin and some other minor constituents. In order to meet the energy demand, the feedstocks are categorised into first generation, second generation and third generation (Sharma et al. 2017; Joshi et al. 2020).

First-generation feedstocks include primarily edible plants' parts rich in sugar (sweet sorghum, sugar beet, sugarcane, etc.), oils (sunflower, olive, coconut, palm, etc.) and starches (potato, wheat, corn, barley, etc.) and are utilised for the first-generation biodiesel and bioethanol production. These feedstocks compete with feed and food crop production and encourage deforestation to make more agricultural land making the feedstock unsustainable. However, second-generation feedstocks

contain agro-industrial and forest waste/residues, non-food oil-based plants (Kapok, *Camelina*, rubber, Jojoba, *Jatropha*, etc.) and lignocellulosic biomass (inedible crops like switchgrass, reed canary grass, etc.). These second-generation biomass feedstock sources are plentiful, like rambutan seed, mango peel, coffee cut stem, acai seed, cut stems, husk and pulp of several plants, peanut hull, etc. The third generation consist of microalgae and cyanobacteria which shows high lignocellulosic production. Although these feedstocks show great potential, they still remain in their early stage and require intense study. The agricultural residue and food waste that are increasing enormously due to growing population are encouraged to be used as potent feedstocks for valorisation.

The first and important possibility in declining the agriculture and food waste is to preclude waste generation. The next possibility is to reuse-reduce-recycle and have sustainable management of food and agricultural wastes. The best possibility is to reduce and prevent the food waste, but as per food waste management method, valorisation can also be considered one of the methods where the food waste is enrooted to feed and food products and also food waste is converted to extracted feed and food ingredients, in view of food waste's composition, quantity, robustness and quality.

Being cheap and renewable lignocellulosic source, food and agricultural waste can be utilised to obtain biofuels, antioxidants, novel biodegradable products, enzymes and other commercial materials (Plazzotta and Manzocco 2019). Lignocellulosic biomass consists of lignin (10–25%), hemicellulose (20–40%) and cellulose (40–60%) as phenolic compound.

Lignin majorly helps in maintaining plant structural integrity and consists of *p*-coumaryl alcohol, monolignols, sinapyl alcohol and coniferyl alcohol. The monolignols form three units: guaiacyl (G), syringyl (S) and hydroxy phenyl groups (H). Lignin is related to xylan via various types of covalent linkages like ester linkages between ferulic acid or *p*-coumaric acid and arabinofuranosyl residues and glycosidic linkages between *p*-coumaric acid and xylopyranosyl. Lignin degradation is difficult as it is optically active and insoluble in nature at normal condition. However, at higher temperature (>180 °C) and alkaline or acid hydrolytic treatment, lignin solubilises (Juturu and Wu 2012).

Hemicellulose is amorphous in nature and contains short chained heteropolymers of two or more monosaccharides like hexoses (D-galactose, D-glucose and D-galactose), pentoses (L-arabinose and D-xylose) and some other saccharides (L-fructose and L-rhamnose) (Schutyser et al. 2017). Hemicellulose lacks a crystal structure as it contains its own branched chain and acetyl group (Bhatia et al. 2020). However, it crosslinks with lignin and forms mesh-like structure in order to prevent cellulose from the activity of cellulase. Thus, to get cellulose, the pretreatment of lignin and hemicellulose is required (Joshi et al. 2021).

Cellulose is the major component of lignocellulosic biomass made of linear homopolymeric chain of 1,4-β-D-glucan linked by hydrogen bond forming para-crystalline microfibrils. It provides framework and mechanical support to the biomass. The single unit of cellulose is made of 2000–25,000 glucose monomeric units (Brown et al. 1996). The cellulosic unit comprises high crystalline regions of

50–90% and low amorphous region. The crystalline structure is rigid due to highly ordered structure and is more sensitive to physical stress whereas amorphous region is flexible and accessible to reactant due to poor order of the structure (Reza et al. 2019).

Thus, lignocellulosic biomass obtained from forest residues, agricultural wastes, dedicated energy crops and industrial waste, such as paper and pulp industries and wood industries, act as potential source for valorisation. In spite of burning and dumping, it is efficient to divert the waste towards innovative and holistic sustainable green approach adding value to these wastes and protecting the natural asset.

19.3 Valorisation of Agricultural Residues into Different Bio-Commodities

According to the Food and Agriculture Organization (FAO) definition, food waste refers to the decrease in the quantity or quality of food resulting from decisions and actions by retailers, food service providers and consumers (Gustafson 2019). These agricultural or food wastes impose negative impacts on environment, economy and society (Capanoglu et al. 2022).

Agricultural residues include crop wastes of vegetables, fruits, corn stalks, grain husks, sugarcane bagasse, molasses, roots, leaves of pineapple and banana and banana peels which are mainly left on the fields after harvest or post food processing in food industry (Adhikari et al. 2018). Agro-industrial wastes have the ability to produce substantial number of valuable products which constitute fuels, chemicals, energy, electricity, biopolymers, biofertilisers and by-products (Islam et al. 2021). Food and agricultural wastes contribute various kinds of negative impacts to the world; mainly they affect the total economy and social and environmental problems of an area or the entire world. To minimise the negative impact of agricultural food wastes, various steps have been initiated. Through trial-and-error methods, various valorisation methods have been adopted in order to alter the impact of agricultural or food wastes.

19.3.1 Conversion of Wastes into Fuels

Through the process of pyrolysis, agricultural wastes could be converted into different forms of bio-oil and biochar. These products are obtained through thermal conversion of solid wastes in absence of oxygen (Cusenza et al. 2021). The bio-oils and biochar can be used as an alternative source of petroleum-based products like fuels, chemicals and activated carbons (Adhikari et al. 2018; Varjani et al. 2019) (Table 19.1).

Table 19.1 Biorefinery products from different sources of agricultural wastes

Agricultural wastes	Process used	Products obtained	References
Saw dust	Enzymatic hydrolysis	Bioethanol	Alio et al. (2021), Yaashikaa et al. (2019)
Corn fibre	Enzymatic hydrolysis	Bioethanol	Zhang et al. (2021)
Corn stover	Saccharification and solid state fermentation	Bioethanol	Buruiana et al. (2014), Yaashikaa et al. (2022)
Pomegranate peels	Fermentation using *yeast*	Bioethanol	Talekar et al. (2018), Yaashikaa et al. (2022)

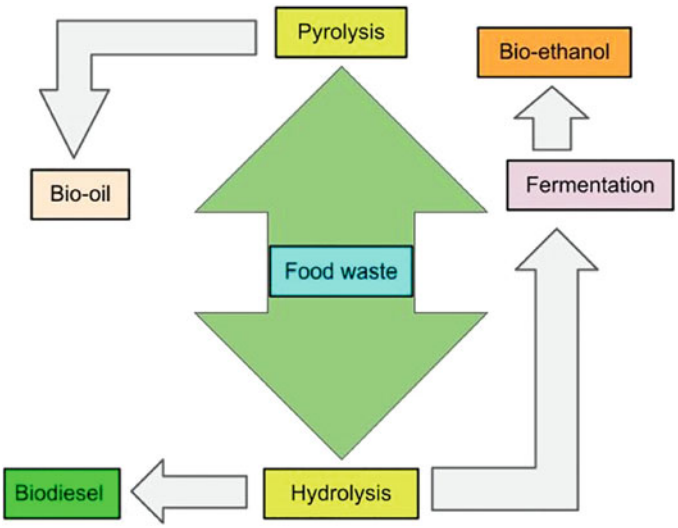

Fig. 19.1 Conversion of food wastes into different bio-commodities

Biodiesel could be produced from agricultural wastes by obtaining the lipids through fungal hydrolysis of food wastes (Fig. 19.1). These lipids are then trans-esterified to produce biodiesel (Karmee and Lin 2014; Joshi et al. 2022).

19.3.2 Production of Valuable Biomaterials

Various enzymes can be obtained from different types of food wastes and by-products by using different kinds of fungal strain (Table 19.2).

Table 19.2 Various enzyme productions from agricultural residues

Wastes	Processes	Organisms used	Biomaterials obtained	References
Coffee waste	Fermentation	*Neurospora crassa*	α-Amylase	Murthy and Naidu (2010)
Food waste	Submerged fermentation	*Aspergillus niger*	Glucoamylase	Wang et al. (2008)
Melon waste	Solid state fermentation	*Bacillus coagulans*	Lipase	Alkan et al. (2007)
Kimchi cabbage waste	Simultaneous saccharification and fermentation for 24 h	*Lactobacillus sakei* and *Lactobacillus curvatus*	Acetic acid	Kim et al. (2018)
Bread waste	Solid state fermentation	*Aspergillus awamori* and *Aspergillus oryzae*	Succinic acid	Leung et al. (2012)
Food waste	Bio treatment	*Hermetia illucens* (black soldier fly)	High-quality animal feed	Magee et al. (2021)
Banana peel	Fermentation	*Trichoderma viride*	Cellulase	Sun et al. (2011)
Coconut oil cake	Fermentation	*Penicillium rugulosum*	Insulinase	Dilipkumar et al. (2014)
Apple pomace	Fermentation	*Aspergillus niger*	Mannanase	Yin et al. (2013)

19.3.2.1 Production of Biopolymers

Biopolymers are known as a unique class of polymers that are eco-friendly and easily biodegradable (Binoj et al. 2017). Biopolymers are synthesised from algal residues or plant-based agricultural waste which contains lignocellulosic fibres, cellulose esters, polylactic acids and polyhydroxyalkanoate (Maraveas 2020; Mal et al. 2022). It was found that plant wastes of pineapple, sisal and jute contain significant amounts of lignocellulosic fibres, which are used as precursors of bio-based polymers (Satyanarayana et al. 2009).

19.3.2.2 Production of Cellulose Nanofibrils

Nanocellulose has recently gained much attention due to its optical properties and high strength, and it is biodegradable in origin (Khiari 2017). Nanocellulose could be obtained by using banana rachis, wheat straw, soy hulls and bagasse and from *Prunus amygdalus* stem residue (FAOSTAT (Food and Agriculture Organization Corporate Statistical Database) data).

19.3.2.3 Production of Biofertilisers

Different levels of nutrients are required in soil for proper development of crops and plants. However, chemical fertilisers used in plants are not only altering the natural ecosystem but also degrading the soil nature and its ecosystem. The agricultural waste contains the same levels of nutrients like nitrogen, phosphorus and potassium which not only enhances soil fertility but also increases the yields without altering natural ecosystems (Mohanty 2021).

Biofertilisers using agro waste compost mixed with microorganism inoculants like *Azospirillum* and *Azotobacter* could be used as an alternate resource against chemical fertilisers (Fig. 19.2).

Agricultural waste management is one of the core approaches to produce green, cost-effective and value-added products in order to minimise the level of biological wastes all over the world. Various methods like the biofuel, biofertilisers, biomaterials and biopolymers are some of the novel approaches to alter the use of synthetic products. However, a significant amount of research and development is required to make the changes sustainable.

19.4 Advancements in Agricultural Residue Valorisation Through Nanotechnology

Lignocellulosic residues are an important resource with a wide range of applications and high potentiality. These residues can be converted to value-added products by following the circular economy concept. As discussed in the above sections, through

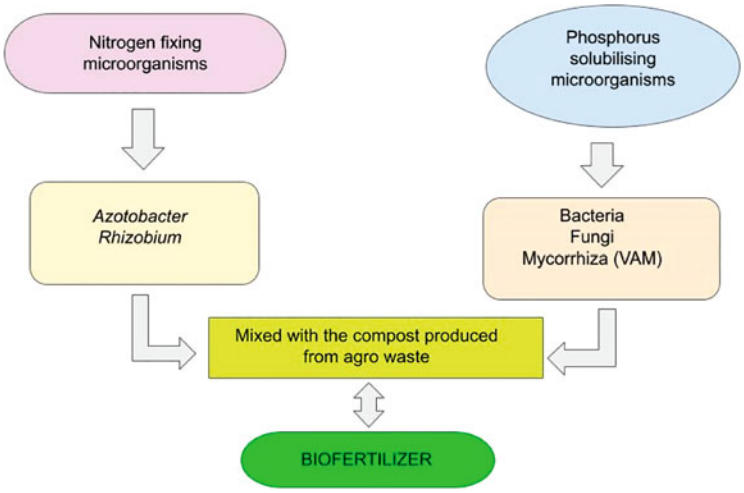

Fig. 19.2 Production of biofertiliser using agricultural wastes

different pretreatment methods, the organic part of the biomass has been extracted which can further be converted into nanoscale form, presenting many more exploitable features with respect to their bulk counterparts, such as higher strength and rigidity, as well as a good reactivity, a large exchange surface (greater area/volume ratio), etc. The components of plant cells, that is, cellulose and lignin, are being considered as potential nanocarriers for active ingredients or in combination with agri-food sector applications such as the following: in case of plant disease management, these nanoparticles play an important role in decreasing the toxicity and increasing efficiency of pesticides (nanopesticides). These nanopesticides are well known for increasing the solubility of a poorly soluble ingredient and easing the release of active products slowly. The major advantage of these nanomaterials depends on the fact that the reactivity takes place at the nanoscale as compared to their bulk counterparts, thus using a low quantity of nanopesticides and also enhancing effect on crop protection. Nanomaterials derived from lignocellulosic biomass show their applicability in the case of enzymatic-based or catalyst-based treatment of biomass in an eco-friendly and economically viable way for high yield of fermentable sugars for the generation of biofuel. In the current scenario, different types of industrially valuable products, reducing sugars and biofuel are being produced with the help of different types of nanomaterials such as metal oxide nanoparticles, carbon nanotubes, etc. (Roy et al. 2021).

19.4.1 Cellulose Nanocrystals (CNCs)

Cellulose $(C_6H_{10}O_5)_n$ is a biopolymer/polysaccharide of glucose moieties, which is mostly present in plants as one of the major components apart from lignin and hemicellulose. It is the most abundant biopolymer on Earth. In plant secondary cell walls, cellulose microfibrils are arranged in parallel to each other. The cellulose microfibrils are approximately 30 nm in diameter consisting of amorphous and crystalline regions, and because of these staggering regions, the overall structure of cellulose is strong. Because of the physical, chemical and biological properties of cellulose, it can be used at the nanoscale level, that is, production of nanocellulose which can be used for the production of nanodevices and high-performance nanosystems. With the advancement in the sector of nanotechnology, nanocellulose has received a great deal of attention as a new bio-based nanomaterial with excellent optical properties, high strength and specific surface area. Nanocellulose can be extracted from lignocellulosic residues and can be chemically tailored for a variety of uses in the field of nanocomposites. A wide variety of crops and lignocellulosic residues such as soybean peel, straw, sugar beet pulp, potato pulp and suede are already being used as raw materials for new low-cost processes for the production of nanocellulose (Sukirtha and Saranya 2020).

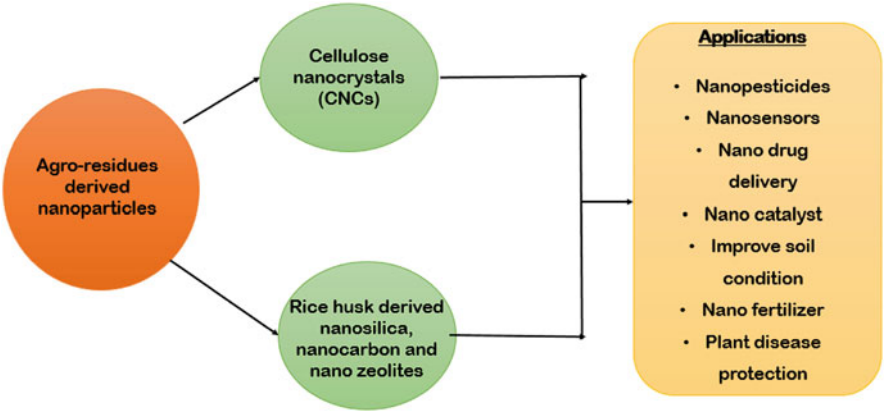

Fig. 19.3 Schematic representation of recent advances in nanoparticles derived from agricultural residues

19.4.2 Rice Husk-Derived Si Nanomaterials

The reuse of agricultural waste has attracted interest in various fields in ecological and industrial aspects. During the whole process from rice plantation to final product, approximately 20% of the husk remains as waste, which is also known as rice husk (RH). Generally, RH is considered to be rich in nanosilica (NS), nanocarbon (NC) and nanozeolite (NZ). It has been reported that rice husk ash is composed of 60% silica and around 40% carbon along with some other minerals. Rice husk ash (RHA) is composed of 60% silica and 10–40% carbon and other minerals. Advance techniques help in the production and extraction of nanocarbon and nanosilica from rice husk and rice husk ash. The extracted nanosilica is further used for the production and development of nanozeolites (NZ). These nanoparticles have various applications in industries and also in an environmental aspect, for example, electronics, ceramic, adsorbent, antimicrobial products, bio-sensing and biomedical applications, etc. (Ali et al. 2021) (Fig. 19.3).

19.5 Challenges and Future Prospects in Agricultural Residue Valorisation

Lignin-poly (ethylene glycol) methyl ether methacrylate hydrogel, lignin-chitosan alkali lignin hydrogel, lignin nanoparticle-poly (acrylic acid) hydrogel and others have been studied for their nontoxic nature and biocompatibility to human cell lines. Cheng et al. recently created lignin-based nanomicelles that were biocompatible for oral drug administration (Cheng et al. 2020). Researchers have demonstrated the potential of tetracycline and curcumin for PLA-lignin composites

(Domínguez-Robles et al. 2019) and nanofibers made of poly (vinyl alcohol)-lignin loaded with Ag nanoparticles for uses in wound healing (Aadil et al. 2018). Lignocelluloses attracted the consideration of the scientist in recent decades as a plentiful resource for the synthesis of second-generation ethanol and other derivatives. This section discusses the challenges in the utilisation of lignocellulosic biomass from agricultural residues through nanobiotechnological techniques.

19.5.1 Recovery of Immobilised Enzyme

The cost of the procedure is determined by the enzyme's capacity to be separated and reused; recovering the enzyme is essential in industrial applications because it lowers costs. It is simple to recover enzymes from reaction mixtures that have been immobilised on chitosan and calcium alginate (Chagas et al. 2015; Gholami-Borujeni et al. 2011). Centrifugation has been used in separation processes using nanoscale support because the immobilised enzyme at the nanoscale makes it difficult to recover the enzyme using the standard method. This makes the process laborious, inconvenient and time-consuming (Valerio et al. 2013). The super paramagnetism feature of iron makes it feasible to extract easily from the reaction media by external magnetic forces, and this can be addressed by utilising the magnetic nanoparticles (Fe_3O_4 and maghemite, Fe_2O_3). Because of their outstanding qualities, such as a high surface-to-volume ratio, lack of toxicity and strong biocompatibility, magnetic nanoparticles are perfect for immobilising enzymes. Furthermore, external diffusion issues are not an issue for magnetic nanoparticles, which are non-porous nanoparticles; they are more suitable for industrial applications (Xu et al. 2014).

19.5.2 Nanotechnology and Enzyme Compassion

Numerous studies have been conducted to examine and comprehend the unique characteristics of both enzymes and nanomaterials (Giardina et al. 2010). After immobilisation, enzymes might lose diffusional mobility and experience structural changes, making it challenging to pinpoint the precise origin of the alteration. There is currently no clear answer for how to set up an experiment to distinguish between these two impacts of conformation modifications and diffusional mobility (Johnson et al. 2014). For phenolic compound oxidation, Pang et al. immobilised laccase on carbon nanomaterials in their study (Pang et al. 2015). To examine the secondary structure of laccase following immobilisation, they used circular dichroism spectroscopy. Despite the fact that the nanomaterial used was quite similar to that in the earlier study by Zhang et al., they discovered that there had been no appreciable conformational change in the immobilised laccase and concluded that substrate accessibility rather than conformational change was to held responsible for the decline in enzymatic activity (Zhang et al. 2013). These investigations have

demonstrated, in brief, that immobilising various enzymes on various nanomaterials would result in a system that may be unique from others. Scientists still have very little understanding of how enzymes with nanomaterials behave. Therefore, by concentrating on how to examine the effectiveness of specific factors, more effort should be made to comprehend enzymes incorporated in nanotechnology.

19.5.3 Commercialisation of the Implementation

As the majority of investigations are carried out at the lab scale, it is still unclear if it is feasible to use a nanotechnological approach to lignocellulose valorisation. Because the actual performances of the nanomaterials in treating lignocellulosic waste could differ from the findings achieved in the laboratory, it is challenging to determine the ideal circumstances in the bioremediation of agricultural wastes when it comes to the actual field applications. Developing lab-scale experiments for practical use would be the main obstacle.

19.5.4 Nanomaterials and Protracted Durability

Employing nanoparticles can be seen as sustainable in the sense that there are no environmental issues throughout the life cycle. A number of negative impacts when exposed repeatedly over an extended period of time including transient inflammation, skeletal anomalies in foetuses and bone resorption in SWCNTs were reported (Kobayashi et al. 2017). According to Viana and team, creating TiO_2 nanoparticles involves centrifugation followed by intense heating at 200–1100 °C and incorporates high cost in the biorefinery (Viana et al. 2010). The goal of treating dye effluents is contradicted by the use of free nanoparticles in wastewater treatment, which carry the risk of adding additional pollution to the effluent which was already polluted. Immobilisation supports are therefore required to avoid these problems (Nadaroglu et al. 2017). In conclusion, because of their potential use as powerful catalysts, nanomaterials like nano-Zn, AgNPs and nano-ZnO are extremely sustainable. Due to their nontoxic and environmentally benign qualities, they are less damaging to humans and the environment than TiO_2 and CNTs. Although photosensitive semiconductors like ZnO and TiO_2 can save resources like water, chemicals and cleaning agents (Rauf et al. 2011), more research on the sustainability of nanomaterials is still needed because photocatalysis is not cost-effective because it consumes more energy from UV light and can only be used in a limited ultraviolet range (Tan et al. 2015).

Excellent results were obtained from the dye decolourisation investigations carried out using hybrid nanoflowers. Ge et al.'s method for synthesising the hybrid nanoflowers requires 3 days for the reaction to take place at room temperature, despite the fact that hybrid nanoflowers can attain increased enzymatic activity,

reusability and stability (Ge et al. 2012). The broad use of these nanoflowers has been significantly limited by the length of time required. Therefore, a new strategy is required to hasten the synthesis of nanoflowers so that it can be used in more industrial applications. The first significant decrease in synthesis time, from 3 days to only 5 min at room temperature, was made by Batule et al. in their work (Batule et al. 2015).

The biorefineries stand out as the most ideal business platform to create the essential chemical changes in relation to lignin valorisation and the circular economy. The production yield can be increased by using heterogeneous feedstock. However, the amount of lignin, cellulose and hemicelluloses should be considered when choosing waste biomass to utilise as feedstock. The amount of acid loading, duration of hydrolysis, temperature and any chemical, mechanical or enzymatic pretreatments used all have an impact on the type and nanoscale of the products produced by biorefineries. Upon producing high value-added products in a nanocellulosic biorefinery, the utilisation of collective cellulosic wastes from industrial and agricultural operations appears as the most economical and energy-efficient option. Future biorefineries should consider using heterogeneous feedstocks to increase the production of various products with added value. The choice of an enzyme and the mechanisms involved in its regeneration will be essential for the economic management of biorefinery operations. New bioagents, reactor designs with improved mass transfer of the substrates into the end products, redesigned enzymes with enhanced activity and better liquid and gas separation techniques are needed for the biochemical method to be economically viable. In order for it to be applied in prospective biorefineries, further study is required to identify the process parameters that will make this possible. To measure the major cost generation and competitiveness of technical breakthroughs, an assessment of the cost of the technology is required.

19.6 Techno-Economic Analysis for Agricultural Residue Valorisation

The techno-economic analysis (TEA) for nanotechnology-based agricultural residue valorisation initiates from the conventional process and simulation. It is indispensable to assess the techno-economic (TE) analysis for the bio-product production from agricultural residues to know the process framework in relation to the circular economy. It also aids in understanding the industrial viability of any method and various operational conditions that influence the cost of production (Singh et al. 2022; Kushwaha et al. 2022). Mostly, SuperPro Designer® and Aspen Plus® are employed for the TEAs (Yang and Rosentrater 2019; Bbosa et al. 2018; Ruddy et al. 2019). The model based on Aspen Plus® for the conversion of corn stover and agricultural residue by dilute acid pretreatment to bioethanol have been extensively quoted and used as a standard for the techno-economic assessment for other

bioenergy generation processes (Humbird et al. 2011). TEA is analysed by investment, process capacity, biomass, product, operational and land expenses and profits (Hussain et al. 2021; Bajgai et al. 2022). The estimation of equipment expenses and project investment is assessed by Aspen Icarus/ASPEN Plus software (Ge et al. 2021). The process modelling tools helps to generate an efficient model to operate a complex biorefinery with numerous recycle loops, which will help in capturing the difficulties and potential for incorporating wastewater treatment, functions for controlling heat and cooling system (Meramo-Hurtado et al. 2020).

Recently, efforts have been carried out to develop simple publicly available models which does not need any experienced person for operation as in traditional software. For example, a spreadsheet tool called Early State Technoeconomic Analysis, version 2, was released aiming precisely at hybrid biological/catalytic process (Viswanathan et al. 2020) and corroborated outcomes for sorbic acid and corn ethanol production with SuperPro Designer® simulations, displaying minimum selling price (MSP) variation of 3–22% compared to the published values. Further, another Python-based model called Biorefinery Simulation and Techno-Economic Analysis Modules was used for comparing the results of lipid-cane-derived ethanol and biodiesel co-production (modelled in SuperPro Designer) and corn stover for ethanol production (modelled in Aspen Plus). Depending on the data input origin, details given in unit operations and accuracy of thermodynamic model used, the modelling methods' accurateness, dependability, efficacy and scalability vary.

Lightweight TEA models are used to evaluate cost and mass balances for processes with a few unit processes and recover streams. However, the restraint of such simplified process models is their capability to precisely forecast the remaining steam and electricity requirements. Although it has a negligible influence on minimum selling price (MSP) owing to less fuel and power charges (Cortes-Peña et al. 2020), energy equilibriums are the significant inputs towards greenhouse gas (GHG) life cycle inventories (Baral et al. 2019a).

19.6.1 Economic Metrics

A significant gap occurs amid how research community and private industries use TEA. The TEA is used to inform and prioritise development and optimisation processes to emphasis on total capital investment (TCI or CAPEX), yearly operating cost (AOC or OPEX) and MSP after cash flow analysis (Baral et al. 2019b). MSP is analysed depending on the unit price desired to gain a net present value (NPV) of zero for a traditional facility, with internal rate of return (IRR), which is 10% for bio-refineries (Humbird et al. 2011). In comparison, private industries looking to assess possible investments are generally normally using simpler profit-related pointers where revenues are not taken into consideration (Eq. 19.1), gross margin (Eq. 19.2), return on investment (Eq. 19.3) and payback period (Eq. 19.4) (Goswami et al. 2022; Scown et al. 2021).

$$\text{Revenue}(\$/\text{year}) = \text{Product sales}(\text{kg/year}) \times \text{Product selling price}(\$/\text{kg}) \quad (19.1)$$

$$\text{Gross margin}(\%) = \frac{\text{Annual revenue}(\$) - \text{Annual operating cost }(\$)}{\text{Annual revenue}(\$)} \times 100 \quad (19.2)$$

$$\text{Return on investment(ROI)}(\%) = \frac{\text{Annual net profit}(\$)}{\text{Total capital investment}(\$)} \times 100 \quad (19.3)$$

$$\text{Pay back period}(\text{year}) = \frac{\text{Total capital investment}(\$)}{\text{Annual average net flow}(\$)} \quad (19.4)$$

19.7 Conclusion

Due to its widespread availability and ease of access, lignocellulosic biomass can serve as a consistent supply of feedstock for the biomass valorisation process. The use of energy-rich components like cellulose and hemicelluloses is hampered by the presence of lignin in lignocellulosic biomass. As a result, biomass can be valued either through pretreatment, which involves removing lignin and using it in various industries, or through hydrolysis, which involves breaking down complex components like cellulose and hemicellulose into simple sugars for use in the production of fuels and chemicals. Utilizing lignocellulosic materials to produce a variety of fuels and goods through effective nanobiotechnological pathways has the potential to change the global energy landscape.

The chapter reviewed the agricultural biomass valorisation into various bio-products. In order to comprehend the underlying process, agricultural residue valorisation in the field of major nanobiotechnology has been discussed. Critical description of the conversion of lignocellulosic biomass into different products using NMs and biocatalysts was also covered. In addition, the appropriate scientific literature was studied to examine the use of biomass valorisation based on nanobiotechnology in the circular bioeconomy. Additionally, we spoke about a few challenges with biomass valorisation based on nanobiotechnology, as well as alternatives and recommendations for how to solve them. The greatest difficulty that still has to be overcome is the fine-optimisation of pretreatment procedures for various biomass varieties in order to attain the highest level of techno-economic viability.

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Chapter 20
Biogas Energy from Animal Waste

Zuhal Akyürek

Abstract The continuous rise in the global energy demand, depletion of fossil fuel reserves, and increase in global greenhouse gas (GHG) emissions have raised the attention on utilization of renewable energy sources. Conversion of organic waste into renewable energy can be a sustainable solution option to meet the future energy demand while providing numerous environmental benefits. Anaerobic digestion (AD) process refers to biochemical degradation of organic materials. Biogas is a colorless and odorless flammable gas produced from anaerobic digestion process of organic materials such as urban, industrial, livestock, and agricultural wastes. AD has become as one of the most favorable renewable energy pathways for utilization of animal waste. Livestock waste is a problematic waste that contributes to anthropogenic GHG emissions. Hence, energy conversion of animal waste provides many advantages. Energy production from animal waste enhances solid waste management strategies by reducing generated waste volume, controlling methane emissions from landfilling applications, protecting the human and environmental health by inhibiting odors and pathogens, and producing digestate as organic fertilizer to improve soil fertility. Biogas production provides production of green power with net zero CO_2 emissions. Methane is a more effective GHG than carbon dioxide. Controlled methane production from animal waste through biogas technology has utmost significance to mitigate global warming and to produce sustainable energy. This study covers the biogas production from animal waste, influencing factors on biogas formation, electricity generation from biogas and multiple benefits of biogas energy to human beings and environment.

Keywords Animal waste · Biogas · Energy · Environment · Sustainability

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20.1 Introduction

Depletion of fossil fuel resources and rising public concerns on energy security, environmental pollution, and climate change have increased the awareness on environmentally friendly energy resources together with sustainable conversion technologies. The risen population growth has boosted the energy consumption resulting from the industry, buildings, and transportation sectors, and more renewable resources need to be activated to meet this growing energy demand in an environmentally friendly manner (Joshi et al. 2020, 2022). The biomass-/waste-based power generation can play a crucial role in establishing the green economy and replacing fossil fuel-based energy resources on large-scale applications (Scarlat et al. 2018). Global GHG emission has gradually increased in the last decade (Fig. 20.1) and reached to 36.3 billion tons in 2021 (IEA 2022). To limit the increase in global temperature below 2 °C and to mitigate climate change urgent actions are required.

The livestock sector is a significant contributor to global anthropogenic greenhouse gas (GHG) emissions with methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) release to the atmosphere. The distribution of the emissions from livestock supply chains is demonstrated in Fig. 20.2. Livestock has high impact on climate change that livestock production accounts for 15% of the global GHG emissions (Gerber et al. 2013). Animal manure is the by-product of livestock farming. Manure management is very important for recovery of the nutrients and production of energy from animal manure and for reduction of emitted GHG for environmental protection.

Animal waste threatens environment when deposited on land or decomposed in the open dumbs. The poor management of livestock waste results in accumulation of

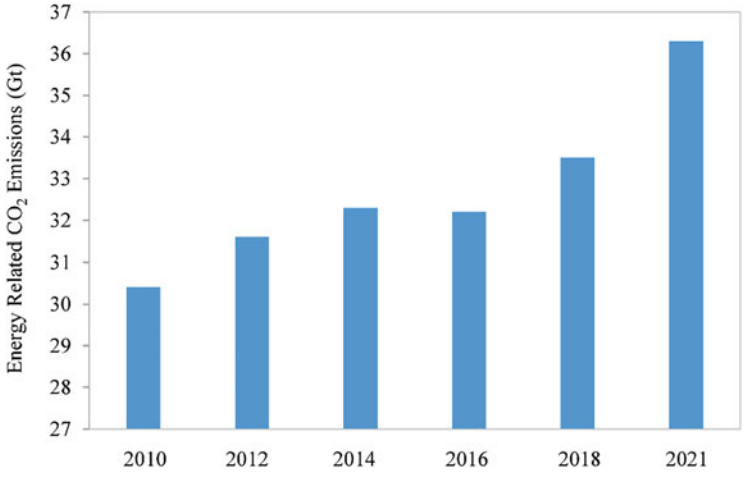

Fig. 20.1 Energy-related CO_2 emissions in the world (International Energy Agency, IEA 2022)

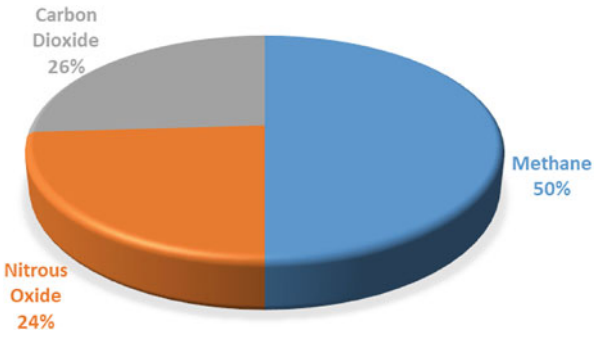

Fig. 20.2 The share of methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) emissions from livestock supply chains (FAO Global Livestock Environmental Assessment Model (GLEAM); Gerber et al. 2013)

excess amount of nutrients and pathogenic microorganisms in soil, water eutrophication, and air pollution caused by emitted greenhouse gases (Díaz-Vázquez et al. 2020). Manure storage also results in unpleasant odors and pathogen formation. Animal manure can cause serious infections both in animals and in humans through direct contact with animal wastes or through contaminated food or water (Manyi-Loh et al. 2016) and threatens animal and public health. Livestock waste contributes global warming by being a direct source of methane and nitrous oxide ammonia emissions into the atmosphere (Wolter et al. 2004). Methane is 28 times more effective GHG than carbon dioxide over a 100-year period. Hence, it requires to be strictly controlled. Animal manure loses about half amount of its ammonium content during handling and storage, which contributes acid rain and deteriorates ecosystem and biodiversity (Masse et al. 2011).

Huge amounts of manure produced could be used as a cheap source of bioenergy (Silwadi et al. 2022; Akyürek 2021; Xing et al. 2020). Several technologies could gain the energy potential from manure, including direct combustion, fuel densification, pyrolysis, composting, and anaerobic digestion (AD) technology. Direct combustion animal manure can be a possible option only after drying process. This method is usually not feasible for high moisture content manures. Densification and pelletizing of the animal waste by applying certain pressures and temperatures also require getting rid of the moisture content of the fuel (Mazzu 2007). Dewatering manure is an expensive procedure, and in addition, it results in formation of undesired wastewater by-product (Wang et al. 2021). Pyrolysis of animal manure is a complex process due to varying reaction mechanisms and reaction rates during component decomposition (Akyürek 2019a). Pyrolysis process is a precursor for combustion and gasification processes; hence, it also requires drying of the feedstock (Oyedun et al. 2014). Composting is another widely used method for manure treatment due to its cost effectiveness; however, it can result in leachates and emissions, which have adverse impact on the quality of air, soil, and water (Magrí and Teira-Esmatges 2015; Peigné and Girardin 2004). Among the alternatives, anaerobic digestion (AD) technology is the most promising option for renewable energy production from animal manure (Bhatnagar et al. 2022). Biogas produced from AD process is a cleaner, safer, environmentally friendly, and readily available fuel compared to fossil fuels (Forssberg 2010; Wang et al. 2021).

In the following section, the details of AD technology, biogas properties, parameters affecting biogas production efficiency, biogas production from animal manure, bioenergy generation potential of animal manure, and environmental impacts of biogas production have been evaluated.

20.2 Anaerobic Digestion (AD) Process

AD refers to biochemical degradation of organic material by bacteria. The main product of the AD process, biogas, is a flammable gas, which can be used for power generation to produce combined heat and power as well as used in transportation sector as vehicle fuel after purification and upgrading (Scarlat et al. 2018). The other end product generated in the AD process is digestate. The digestate can be used as a soil conditioner or organic fertilizer due to its high nitrogen (N), phosphorous (P), and potassium (K) contents (Arelli et al. 2022). The products of anaerobic digestion process are demonstrated in Fig. 20.3.

20.2.1 Biogas

Biogas has become one of the most promising energy forms in the recent decades as natural gas substitute. Biogas can be produced from landfills, wastewater treatment plants, sewage treatment plants, and anaerobic digestion plants processing organic waste.

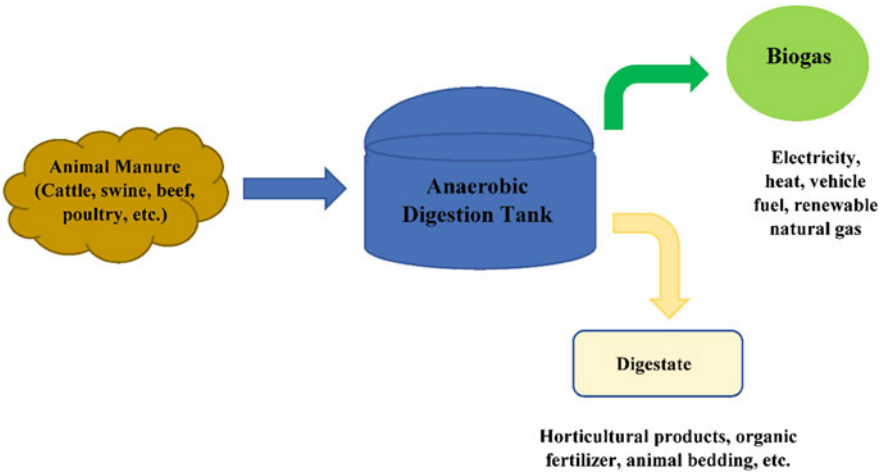

Fig. 20.3 Flow diagram of AD system processing animal manure (EPA 2020)

Table 20.1 Characteristic properties of natural gas, untreated biogas produced from organic waste, and landfill gas (Lyytimäki 2018; Demirbaş 2010; Bond and Templeton 2011; Jönsson et al. 2003)

Composition	Natural gas	Biogas	Landfill gas
CH_4, Vol.%	87–96	60–70	45–55
CO_2, Vol.%	0.1–1.0	30–40	30–40
N, Vol.%	<1	<1	5–15
H_2S, ppm	5.5	10–2000	50–300
HHV, MJ/m^3	35–40	21–24	13–19

Anaerobic digestion process produces higher-quality products with lower environmental impact compared to landfilling gas. In Table 20.1, the comparison of characteristic properties of biogas from organic waste and landfill methane with natural gas is presented. As can be seen from the table, biogas contains higher amounts of methane compared to landfill gas. The heating value of biogas is much higher than landfill gas. Biogas can further be upgraded to bio-methane by carbon dioxide removal to be incompatible with natural gas (Saleh and Hassan 2021). Biogas contains small amounts of contaminant gas, hydrogen sulfide (H_2S), which is very corrosive and toxic. Hydrogen sulfide gas needs to be removed from the system for avoiding operational problems. Hydrogen sulfide also has known to affect the amount and quality of the biogas produced (Farghali et al. 2020).

Biological removal of H_2S from biogas stream is carried out with aerobic bacteria oxidizing H_2S into sulfur (Mamun and Torii 2015). Bioreactors such as biofilters, bio-trickling filters, and bio-scrubbers are generally used to treat H_2S in biogas (Dumont 2015). Alternatively, additives can be used to enhance the AD process and to reduce H_2S emissions. Especially iron (Fe) addition to feedstock as a supplement stabilizes the AD process, improves methane yield, and controls H_2S emissions (Cai et al. 2018; Zhang et al. 2018).

20.2.2 Biogas Production

Anaerobic digestion is biodegradation of organic material in the absence of oxygen by microorganisms. It is a viable treatment solution for animal wastes due to its multiple benefits including green energy production, avoiding water and soil pollution, and controlling GHG emissions to the atmosphere. Anaerobic digestion of animal manure is a useful waste-to-energy (WTE) strategy by reducing the waste volume and revealing the untapped energy potential of manure (Akyürek 2019b).

In anaerobic digestion process, organic waste is converted into biogas through a series of bacterial groups. Anaerobic digestion process consists of four consecutive phases such as hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Figure 20.4 shows the details of each phase (Wang 2014). In the first phase, hydrolysis, complex organic matter of the organic waste decomposes into monomers. Polymers break down into monomers, carbohydrates into sugar, fat into fatty acids and

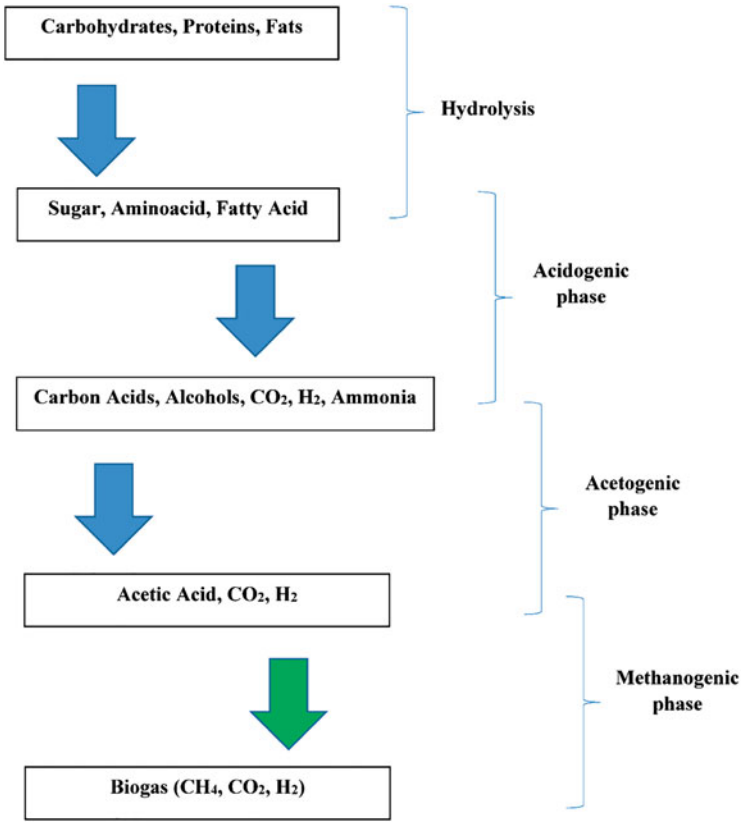

Fig. 20.4 Phases and steps of AD process

glycerol, and protein into amino acid and peptides. It is relatively a slower phase compared to other phases. The rate of hydrolysis phase depends on the substrate which ranges from a few hours to many days. The reaction mechanism for hydrolysis is given as follows (Lohani and Havukainen 2018; Anukam et al. 2019; Zupancic and Grilc 2012):

$$(C_6H_{10}O_5)n + nH_2O \rightarrow nC_6H_{12}O_6 + nH_2 \tag{20.1}$$

In the acidogenic phase, monomers are degraded by microorganism (sugar, amino acids, peptide, fatty acid, and glycerol) into alcohols, hydrogen, carbon dioxide, and organic acid by acidogenic bacteria. The reactions of the acidogenic phase are given below (Lohani and Havukainen 2018; Anukam et al. 2019; Zupancic and Grilc 2012):

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \quad (20.2)$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \quad (20.3)$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad (20.4)$$

In the third phase, acetogenesis, the products of acidogenic phase are converted into acetate and hydrogen. Acetate is used by methanogenic bacteria to produce methane. The reactions that take place during acetogenesis phase are presented in the following equations (Lohani and Havukainen 2018; Anukam et al. 2019; Zupancic and Grilc 2012):

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+HCO_3^- + 3H_2 \quad (20.5)$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (20.6)$$

$$CH_3CH_2OH + 2H_2O \rightarrow CH_3COO^- + 3H_2 + H^+ \quad (20.7)$$

In the final phase, methane-forming bacteria produce methane using the substrate produced in acetogenesis phase (Kumar et al. 2018; Prajapati et al. 2018). The methanogenic bacteria are very sensitive to the changes in the medium. The reaction steps of methanogenic phase are given as follows (Lohani and Havukainen 2018; Anukam et al. 2019; Zupancic and Grilc 2012):

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (20.8)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (20.9)$$

$$2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 3CH_3COOH \quad (20.10)$$

The efficient reduction of carbonaceous pollution can be controlled in the methanogenic phase of AD process through reduced biological oxygen demand (BOD) and chemical oxygen demand (COD) (Bajpai 2017).

20.3 Factors Influencing Biogas Production

AD process has sensitive and complex mechanism that many factors have influence on biogas production efficiency. The major factors affecting the AD process efficiency are composition of animal manure (TS%, VTS%), carbon to nitrogen (C/N) molar ratio, temperature of the reactor, pH, alkalinity, trace elements, organic loading rate (OLR), solid concentration, and hydraulic retention time (HRT) in the reactor. Optimization of these parameters is significant to maximize biogas production with high methane content.

Animal manure can show some compositional limitations to AD process due to its low C/N ratio, total solids (TS), volatile solids (VS), and high proportion of

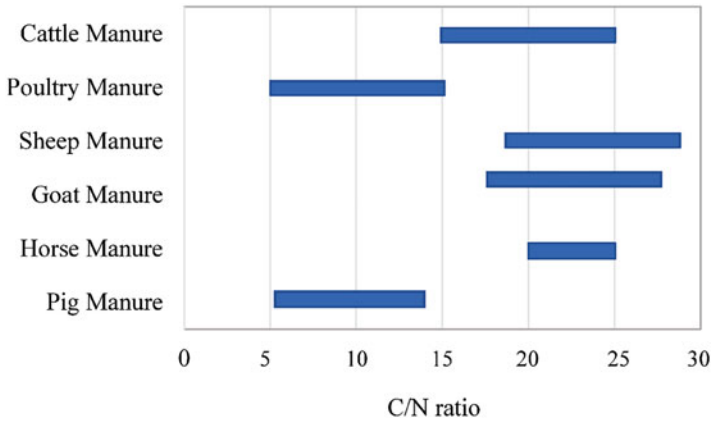

Fig. 20.5 The range of C/N molar ratios (Divya et al. 2015; Zhang et al. 2013)

Table 20.2 Characteristics of different types of animal manure

Waste type	Moisture, %	TS, %	VTS, %	pH	Reference
Cattle manure	42.20	57.80	55.10	7.30	Divya et al. (2015)
Buffalo manure	79.26	20.74	73.85	7.00	Guarino et al. (2016)
Poultry manure	21.18	78.82	48.51	8.70	Carlini et al. (2015)
Sheep manure	69.70	30.30	20.60	7.98	Song et al. (2010)
Goat manure	66.35	33.65	82.21	7.94	Zhang et al. (2013)
Horse manure	76.50	23.50	88.70	7.10	Hadin and Eriksson (2016)
Duck manure	83.60	16.40	13.00	6.82	Song et al. (2010)
Camel manure	63.93	36.07	74.52	7.00	Silwadi et al. (2022)
Rabbit manure	63.10	36.90	25.30	8.05	Song et al. (2010)
Pig manure	28.90	71.10	62.30	5.50	Divya et al. (2015)

lignocellulosic materials (Seppälä et al. 2008; Carlsson et al. 2012; Nasir and Mohd 2015). The feedstock used in biogas production through AD process should provide a suitable environment to ensure high metabolic activity of microorganisms involved in the process (Dobre et al. 2014). Lignocellulosic materials show more resistance to degradation by microorganisms due to their complex structure (Perez et al. 2002; Singh et al. 2014).

The fermentation medium should contain biodegradable organic matter having C/N ratio between 15 and 25. Lower C/N ratios may result in excess amount of ammonia in the medium, which rises the alkalinity in the digester and leads to lower the biogas yield (Uddin and Wright 2021). Animal manure is more appropriate for biogas production compared to agricultural residues which have much higher C/N ratios (Kwietniewska and Tys 2014). Typical C/N ratios of different manure types are given in Fig. 20.5. As can be seen from the figure, cattle manure is a more suitable substrate for AD process. C/N ratio can be altered by co-digestion of manure

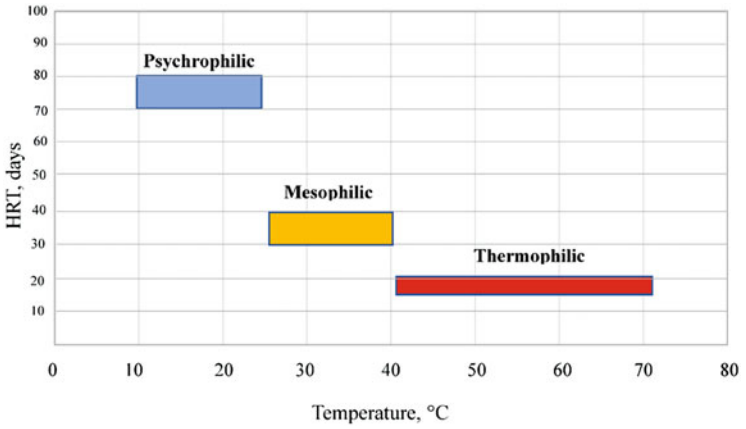

Fig. 20.6 Classification of AD process according to digestion temperature

with agricultural residues. Table 20.2 shows the characteristics of some selected animal manure.

Biogas plants operate optimally at neutral pH level, which is the suitable condition for methane-forming bacteria to produce biogas (Çalışkan and Ozdil 2021). BOD and COD levels are also important factors for methane production (Kwietniewska and Tys 2014). Higher BOD level promotes degradation of the organic matter. AD process is an effective way to reduce COD and BOD levels of the waste.

Temperature has strong influence on performance and stability of AD process and biogas production efficiency (Dobre et al. 2014). AD process can be conducted under three different temperature ranges as psychrophilic, mesophilic, and thermophilic (Teferra and Wubu 2018). Figure 20.6 illustrates the temperature range and HRT of AD.

Thermophilic AD takes place at higher temperatures to increase the degradation rate of feedstock and hence lower the hydraulic retention time (HRT) which normally takes 30–40 days of batch digestion in full-scale operations (Wartell et al. 2012). Thermophilic AD produces higher amount of biogas and provides higher methane yield and lower pathogen levels but requires additional heat input into the digester. AD processing at mesophilic condition produces less amount of biogas compared to thermophilic condition; however, due to its lower operating costs and more robust and stable operation, mesophilic operation is preferred in the commercial AD systems (Labatut et al. 2014; Uddin and Wright 2021).

20.4 The Methane Yield of Animal Manure-Based Biogas

Methane is the major component of biogas and the methane yield of biogas depends on the efficiency of AD process. Methane production from AD process of animal manure varies with volatile solid content of manure (Díaz-Vázquez et al. 2020).

Economically feasible biogas production requires improving the degradation rate and methane yield. Methane yield can be enhanced by increasing the operating temperature and changing the organic loading rates (OLR). Co-digestion of manure with agricultural residues is a possible way to increase the OLR for promoting methane production (Ahlberg-Eliasson et al. 2021). Co-digestion can also improve the digestate nutrient content for better soil conditioning (Akyürek 2018; Ahlberg-Eliasson et al. 2017; Monlau et al. 2015). Methane yields from mesophilic AD of animal manure with possible co-digestion alternatives of agricultural residues are presented in Fig. 20.7. Agricultural wastes have relatively higher high carbon to nitrogen ratio and nutrients that promote bacterial activity (Li et al. 2019) and improve their methane yield compared to animal wastes. The restriction on agricultural residues due to seasonal availability has also led to the incorporation of industrial wastes in anaerobic co-digestion process such as food industry wastes, cheese whey, microalgae, sugar beet by products, fish wastes, etc. having high amount of organic matter for co-digestion (Mata-Alvarez et al. 2014).

20.5 Energy Generation from Biogas

Utilization of organic waste materials to generate energy in the form of biogas has gained more attention in the recent decades due to climate change concerns. Energy generation from biogas seems to be a promising solution to address solid waste management issues to mitigate GHG emissions and protect the environment.

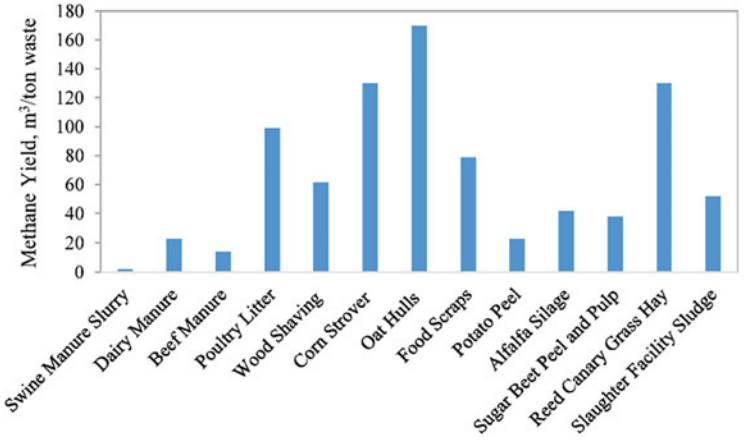

Fig. 20.7 Methane yield of some selected biomass (Moody et al. 2011)

The methane content in biogas determines its calorific value. Typical biogas from an AD process has 6–6.5 kW h/m^3 energy content which is equivalent to 17 MJ/kg calorific value (LHV). Biogas can be directly combusted or upgraded to methane as natural gas. There are several methods for biogas upgrading to biomethane such as water scrubbing (Collet et al. 2017), pressure swing adsorption (Angelidaki et al. 2018), membrane separation (Andriani et al. 2014), amine scrubbing (Chen et al. 2015), etc. Treated biogas can be called renewable natural gas (RNG) or biomethane. Biomethane can easily be stored and injected to the natural gas network or used as vehicle fuel and hence provides diversification of gaseous fuels to contribute global decarbonization targets. Biomethane production and injection to the grid can provide emission savings of 188 kg CO_2/MW h (Savickis et al. 2020). Biomethane is a renewable fuel that can be converted into heat, electricity, combined heat and electricity, motor fuel, and many other products (Pampillón-González and Canepa 2017).

In Europe, biogas is used mostly for electricity production and heating. Biomethane usage in transport sector contributes to about 11% of biogas energy. Upgrading of biogas to biomethane is mostly used in Sweden, the Netherlands, and Germany (Kampman et al. 2017). Figure 20.8 presents the biogas production capacity in European countries.

As can be seen from Fig. 20.8, biogas production prevails in Germany. Germany owns half of the biogas production capacity in Europe followed by the United Kingdom, Italy, France, Czechia, the Netherlands, and Austria. Application of effective feed-in tariff system in Germany allows development of biogas technology (Meyer et al. 2017).

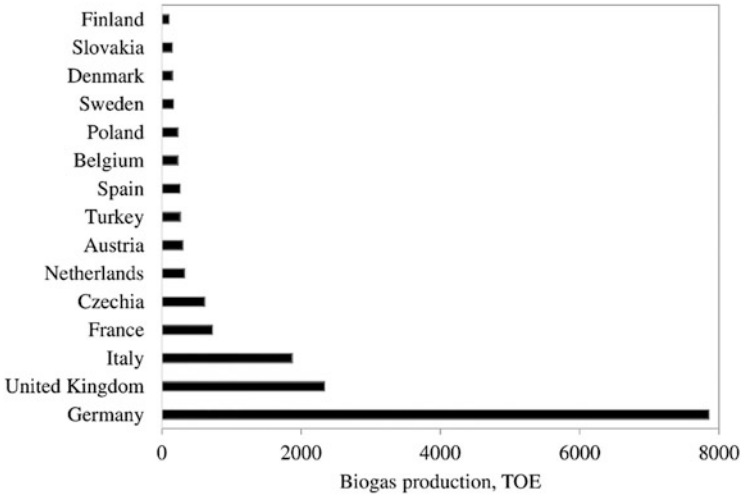

Fig. 20.8 Biogas production in Europe (Eurostat 2019)

20.6 Conclusion

Energy is the vital element of sustainable development. Growing global energy demand, depletion of fossil resources, and concerns on climate change necessitate utilization of renewable sources. Energy production from animal manure offers several benefits in terms of environment and public health protection. Animal manure is a problematic waste that needs to be carefully handled by solid waste management strategies. Animal manure can be converted into energy through anaerobic digestion process. Biogas is a renewable fuel used for power generation and as transport fuel. Biogas production is a viable route for manure management to reduce the waste volume, to control atmospheric GHG emissions from landfills, to avoid odors and pathogens, and to promote a better environment.

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Chapter 21
Recent Trends and Future Prospects of Nanotechnology for Agro-Waste Valorization into Biofuels

Abhishek Joshi and Jaya Arora

Abstract Agro-wastes have the potential to produce biofuels owing to their precise energy-rich components, such as cellulose, hemicellulose, and other biomolecules (carbohydrates, lipids, and extractives). However, robust conversion of agro-waste into biofuels is still difficult due to the complexity of bioprocessing. Biofuels are more sustainable than petroleum fuels, offering good energy competence, lower carbon footprints, and feasible bioprocessing. In the past few years, various nanotechnology interventions have been developed to address this challenge, and metallic, magnetic, and metal oxide nanoparticles (NPs) are now being used to boost the production of biofuels from agro-wastes through their unique active sites for metabolic reactions and processes. One of the advantages of using trace element-based NPs (Co, Fe) is that they can serve as cofactors for hydrogenase and ferredoxin enzymes, which are crucial enzymes for anaerobic processes. In addition, several carbon-based nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and nanosheets, have been proven to be efficient catalysts for enzyme immobilization, thereby improving biofuel production. The current study presents a comprehensive description of nanotechnology applied to agro-waste valorization into biofuels, along with major challenges and future opportunities.

Keywords Agricultural waste · Biofuels · Nanocatalyst · Nanomaterials · Nanotechnology

21.1 Introduction

Nowadays, primary energy consumption is dominated by coal, oil, and gas, leading to sustainability problems including fossil fuel depletion, environmental impacts, and huge price fluctuations (Joshi et al. 2019). Furthermore, global climate change,

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greenhouse gas emissions, and intense energy demand have led to the search for alternatives to fossil fuels (Joshi et al. 2022).

Biofuels offer higher energy efficiency, lower carbon footprints, and easier bioprocessing compared to petroleum fuels (Arora and Ramawat 2013; Joshi et al. 2020). Biofuels can be produced from agricultural waste owing to their rich energy-containing components, such as cellulose, hemicellulose, and other biomolecules (carbohydrates, lipids, and extractives). However, agro-waste conversion into biofuels remains challenging at an industrial scale due to the complexity of the production process (Sharma et al. 2017; Dey et al. 2021).

The use of nanomaterials in biofuel research has emerged as a promising tool in providing cost-effective techniques to improve production quality (Fig. 21.1). There are multiple advantages to using nano-scale materials over other sources for biofuel synthesis due to their size and unique properties such as the high surface area to volume ratio and special attributes such as a significant extent of crystallinity, catalytic activity, adsorption capacity, and stability (Arya et al. 2022). The reports available suggested that nanomaterials used for the purpose of pretreatment and

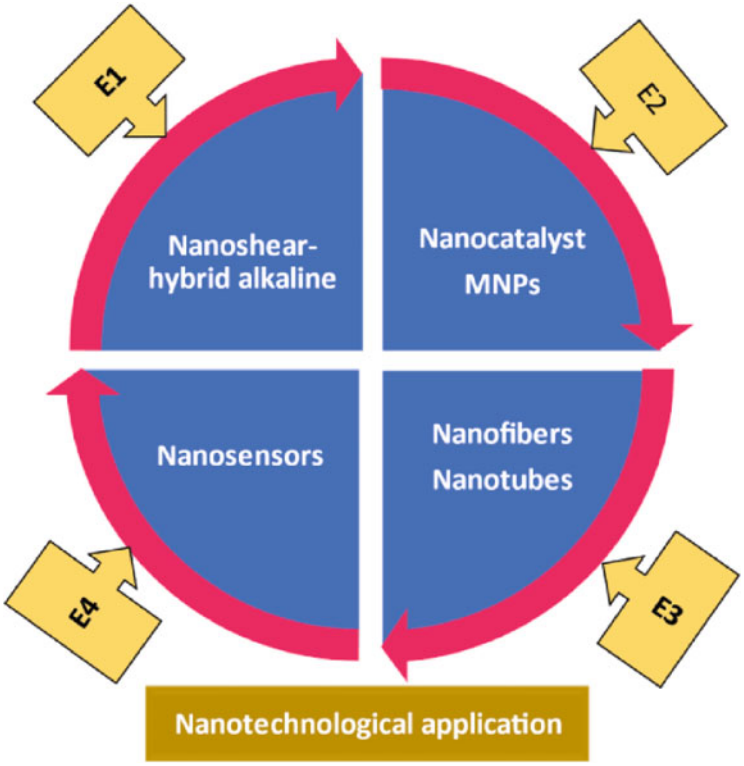

Fig. 21.1 Illustration of the nanotechnological applications in biofuel production process: E1, pretreatment; E2, saccharification/transesterification; E3, purification; E4, detection; and MNPs, magnetic nanoparticles

hydrolysis steps facilitate the molecular chemistry of biomass and release much amount of monomeric and oligomeric sugars (Ingle et al. 2020b). Immobilization of cellulases, hemicellulase, and other catalytic enzymes on nanoscale material increased the rate of hydrolysis and sugar recovery. These immobilized nanocatalysts have been recovered and reused in further hydrolytic reactions, which can make the whole production process cost-effective (Salwan et al. 2020; Chamoli et al. 2020). Metal oxide nanocatalysts also play an important role in syngas production as they reduced tar formation in gasification processes of agro-waste (Nanda et al. 2016). The increased liquid yield was also accomplished by the application of a nanocatalyst of different acids and bases during biomass liquefaction (Vasić et al. 2020). Both the nanoscale and sub-nanoscale instrumentations facilitate the understanding of cell wall ultrastructure as well as the enzymatic mechanism of agricultural residues, which can be useful for the modification of lignocellulosic fiber at the molecular level (de Oliveira et al. 2017). The present paper provides a comprehensive examination of nanotechnology's application to the valorization of agro-waste into biofuel, as well as the major challenges and future prospects.

21.2 Overview on Agro-Waste Types and Their Compositions

Agro-wastes include residues from the production and processing of crops, fruits, vegetables, and dairy products. Agro-wastes can be categorized broadly into three major groups, namely, crop residues, agro-industrial wastes, and livestock wastes (Fig. 21.2).

The crop residues are mostly the waste stuffs generated from the processing of crops at field level, such as leaves, stovers, straws, and seed pods. These residues are the abundant and cheapest organic waste, which can be easily transformed into biofuels and some value-added products. Currently, the global annual estimated production of crop residues is 2802 million tons (Pattanaik et al. 2019). Of these, rice straw, wheat straw, and corn stovers are the most abundant and promising biomasses with a global annual production of 731 million tons, 354.34 million tons, and 128.02 million tons, respectively.

There are other wastes generated from agro-industry production, including vegetable and fruit peels, fruit pomace, waste from sugar manufacturing (bagasse and molasses) and edible oil manufacturing (de-oiled seed cake). The sugarcane bagasse is one of the major agro-industrial wastes with a global annual production of 180.73 million tons (Konde et al. 2021). Other than that, the waste produced from both the edible oil plants (i.e., palm, mustard, soybean, etc.) and nonedible oil plants (i.e., Jatropha, castor bean, etc.) can also be considered as agro-industry wastes.

The third category of agro-wastes include the waste produced from livestock farming practices. This includes liquid manure (urinary waste), solid manure (farmyard manure), and animal fat from slaughterhouses and meat processing industries

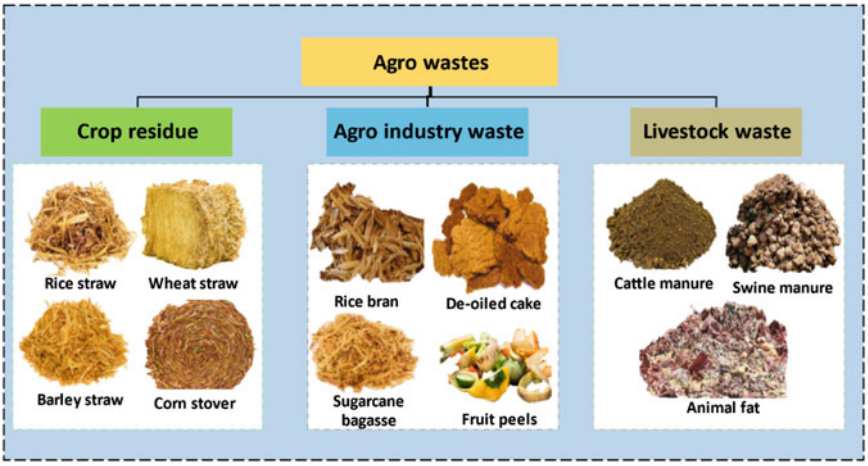

Fig. 21.2 Overview on agro-wastes

(Prasad and Kothari 2022). These wastes are generally considered as useless and are either burnt or flushed directly to the lands and aquatic system. Its incorporation into ecosystems can be responsible for drastic environmental and public health concerns. The livestock sector represents a viable source of waste biomass produced all over world. Various estimates put total global production between 20 and 30 billion tons/year. However, the real figure may be higher, as animals in developing nations are not well fed as those in developed ones (Parihar et al. 2019).

The compositional estimate of biomass is necessary for assessing its potential as a valuable feedstock for biofuel production and for designing the production process (Joshi et al. 2021). Compositional assessment mainly consists of the proximate, ultimate, lignocellulosic, and biochemical compositional analysis (Fig. 21.3). The proximate content represents the quantity of moisture (M), volatile matter (VM), solid content, and ash present in the feedstock. High moisture content has a lower carbon burn rate while the high fixed carbon (FC) and volatile matter represent the high energy and organic content of feedstock and are suitable for rapid thermo and biochemical conversion. The ultimate analysis includes carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) contents, which determine the fuel efficacy of the feedstock (Qian et al. 2021). High C/N ratios also indicate that the feedstock is suitable for the production of biogas and biohydrogen.

The lignocellulosic analysis indicates how much cellulose (CL), hemicellulose (HC), and lignin (L) are present in a feedstock, which are essential and critical for the design and operation of biofuel production process. The higher cellulose and hemicellulose substances are responsible for the cost-effective production of bioethanol, biobutanol, and other bioalcohols. However, high lignin-containing feedstock needs to be pre-treated for the removal of lignin prior to biofuel production

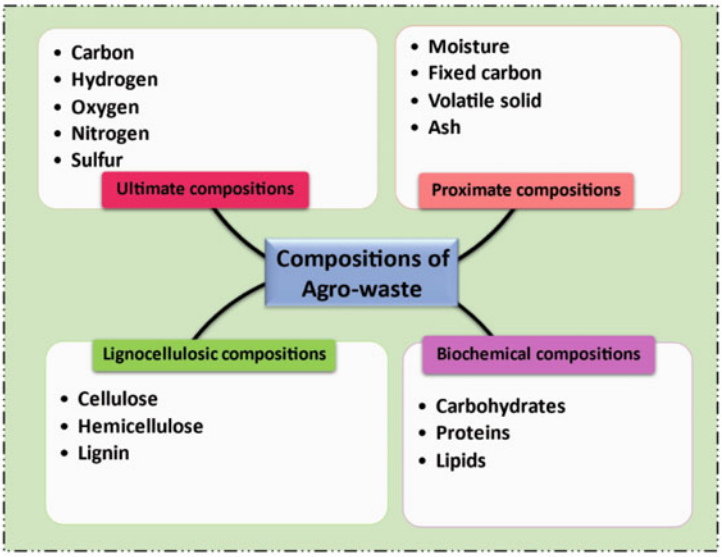

Fig. 21.3 An overview on compositions of agro-wastes

(Joshi et al. 2020). The carbohydrate-rich substrates are also favored for the production of bioalcohol, biohydrogen, and biogas due to its easy degradation properties.

The compositional estimation of diverse agro-waste is provided in Table 21.1. The available reports suggested that the organic and inorganic constituents of agro-wastes are contained in varying amounts according to their origin.

21.3 Recently Enabled Nanomaterials in Biofuel Processes

In the biofuel industry, magnetic nanoparticles (MNPs) have been the top choice for decade because they are able to immobilize enzymes and can be recycled and recuse repeatedly (Fig. 21.4). There have been several attempts to immobilize various hydrolytic enzymes (such as cellulases, lipases, etc.) on MNPs, which have shown improved performance and yield (Table 21.2). Some of the recent studies also proved that MNPs can be coated or modified with various complex materials such as polymers, silica, metallic-organic frameworks (MOFs), and carbon-based materials to enhance nanocatalyst properties and provide potential industrial applications (Shalini et al. 2021; Martínez et al. 2022).

A variety of functionalized NPs have also been reconnoitered for the production of biofuels. Su et al. (2015) demonstrated the efficacy of sulfonated magnetic carbonaceous acid NPs (C-SO_3H/Fe_3O_4) toward hydrolysis of sugarcane bagasse, Jatropha hulls, and plukenetia hulls. The application of this nanocatalyst resulted in

Table 21.1 Compositional analysis of different agro-wastes

Feedstock type	Feedstock name	Proximate composition	Ultimate composition	Lignocellulosic composition	Biochemical composition	Heating value (MJ/kg)	References
Crop residues	Rice straw	M (10%), ash (13.11%), and VM (77.48%)	–	CL (37.9%), HCL (24.1%), and LN (8.75%)	Protein (2.5%)	-	Datsomor et al. (2022)
	Rice straw, rice husk, coffee husk, and cocoa pod husk	M (7.82–12.33%), VM (64.02–72.94%), ash (8–23.7%), and FC (1.92–13.2%)	C (33.5–39.68%), H (4.73–5.60%), and O (52–61%)	–	–	10.49–14.71	Zinla et al. (2021)
	Rice straw	M (8.6%), VM (80.4%) and ash (11%)	C (43.8%), H (6.3%), O (46.1%), and N (0.5%)	CL (38.6%), HCL (24.5%), and LN (3.9%)	–	–	Tsai et al. (2021)
	Wheat straw and wheat hay	M (5.8–7.6%), VM (80.9–82.2%), ash (10.3–13.3%), and SC (92.4–94.2%)	C (41.1–41.8%), N (0.4–0.8%), and C/N (38–99)	CL (30.4–38.6%), HCL (25.8–29.4%), and LN (4.4–7.8%)	Starch (0.5–4.3%), glucose (0.7–2%), and protein (2.8–9.3%)	–	Aramrueang et al. (2017)
	Wheat straw, rice straw, corn stover, rape stalk, and cotton stalk	M (1.08–8.94%), VM (55.82–80.25%), ash (1.81–19.93%), and FC (8.30–27.45%)	C (35–54%), H (3.17–7.94%), O (31–51%), N (0.13–2.23%), and S (0.15–1.44%)	CL (24.91–54.26%), HCL (8.33–32.74%), and LN (10.40–33.36%)	–	12.97–18.58	Niu et al. (2016)
Agro-industry waste	Flower waste (*Hibiscus*, marigold, rose, lily, and jasmine)	M (6.1–12.86%), VM (80–89%), ash (4.35–9.79%), and FC (0.33–0.91%)	C (41–44%), H (6.18–7.28%), O (46.8–49%), N (1.15–2.41%), and S (0.01–0.51%)	CL (28–37%), HCL (19–36%), and LN (1.76–4.54%)	Carbohydrates (16.91–38.84%) and protein (2.19–7.33%)	16–17.2	Dutta and Kumar (2022)
	Jatropha de-oiled cake	M (6.8%), VM (91.5%), and ash (0.65%)	C (44.51%), H (6.9%), N (3.7%), and C/N (12.6)	–	Carbohydrates (23.5%), protein (38.1%), and lipid (7.2%)	–	Sharma et al. (2022)

	Sugarcane bagasse and straw	M (10–10.25%), VM (81.6%), ash (4.57–6.69%), and FC (11.71–13.81%)	–	–	–	16.8–17.8	De Conti et al. (2022)
	Oil bean seed husk	M (6.1–12.86%), VM (80–89%), ash (4.35–9.79%) and FC (0.33–0.91%)	C (47.65%), N (0.1–0.9%), and S (0.1%)	CL (42.34%), HCL (19.2%), and LN (14.47%)	–	19.5	Odetoye and Ocheni (2022)
	Cardoon, grape-vine prunings, and olive pruning	VM (76.2%) and ash (0.71%)	C (41–47%), H (5–8%), and N (1–3%)	CL (29–38%), HCL (15–17%), and LN (17–29%)	–	14.73–19.24	Cavalaglio et al. (2020)
	Sugar beet root, honeydew, sugar beet leaves, and tomato	M (76–94%), VM (5–22%), ash (0.6–3.8%), and SC (5.8–23.3%)	C (39–42.6%), N (0.5–3%), and C/N (21–86)	CL (4–14%), HCL (1.3–18.8%), and LN (0.5–3%)	Starch (0.5–1.3%), glucose (0.3–21%), and protein (3.1–25.6%)	–	Aramrueang et al. (2017)
Livestock waste	Cattle dung	M (84.5%), VM (83.5%), and ash (1.2%)	C (34.5%), H (4.45%), N (1.63%), and C/N (21.1)	–	–	–	Sharma et al. (2022)
	Cattle and pig slaughterhouse wastes	M (26–48%), VM (98%), ash (1%), and FC (0.10–0.27%)	C (51–65%), H (5.6–6.5%), N (1.84–11%), O (27–40%), and S (0.09%)	–	Carbohydrates (1.4–13.86%), protein (1–13%), and lipid (33.25–74.7%)	–	Lee et al. (2021)
	Cow dung	M (86%), VM (64%), ash (11.8%), and FC (18.3%)	C (44.2%), H (4.97%), and S (0.25%)	–	–	17.61	Szymajda et al. (2021)
	Ruminal slaughterhouse waste	M (82%), VM (10.8), and ash (16.2%)	C (2.69%), N (0.14%), and C/N (18.86)	–	Crude protein (17.3%), fat (0.48%), and carbohydrate (47.1%)	–	Omondi et al. (2019)

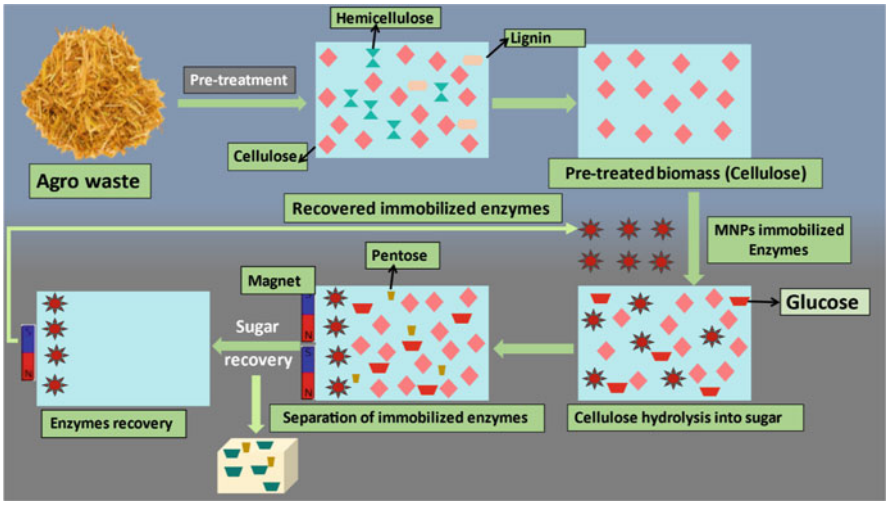

Fig. 21.4 Schematic representation of enzyme immobilization on magnetic nanoparticles and their application in hydrolysis of lignocellulosic biomass; MNPs, magnetic nanoparticles

high glucose and reducing sugar yields. Similarly, Dutta and Saha (2019) reported that xylanase activated magnesium oxide NPs (MgN-xyl) produced 1.82-fold and 1.91-fold increased reducing sugar and glucose, respectively, compared to untreated samples. In another study, Ingle et al. (2020b) applied alkylsulfonic acid functionalized magnetic NPs (Fe_3O_4-MNPs-Si-AS) and butylcarboxylic acid functionalized magnetic NPs (Fe_3O_4-MNPs-Si-BCOOH) toward hydrolysis of sugarcane straw. About 1.10-fold higher sugar yield was reported for Fe_3O_4-MNPs-Si-AS compared to Fe_3O_4-MNPs-Si-BCOOH. The magnetic solid acid nanocatalyst (Fe_3O_4–@C–SO_3H) was also used to hydrolyze palmyra peel and corncob biomass (Rekha and Saravanathamizhan 2021). For both biomasses, applied nanocatalysts produced 97.6% and 90% reducing sugar, respectively.

In addition, few attempts have been made to immobilize enzyme cocktails on metal and metal oxide NPs for hydrolysis of distinct feedstock. Ariaeenejad et al. (2021) immobilized cellulolytic enzyme cocktails (three cellulases, two hemicellulases, and combinations) on the DA/Fe_3O_4NPs@CNC nano-carrier. Application of this nano-biocatalyst in hydrolysis of rice straw and sugar beet pulp showed 20–76% increase in the yield of fermentable sugars compared to the free enzyme cocktails. Moreover, after recovery, about 50% of catalytic activity was maintained up to ten cycles.

Research work has been focused on heterogeneous nanocatalysts, especially for their application in biodiesel production (Feyzi and Shahbazi 2015; Bet-Moushoul et al. 2016). Heterogeneous catalysts, as compared to homogeneous catalysts, are more efficient at separating products and catalysts, eliminate the quenching process, and allow continuous production. According to Ullah et al. (2016), approximately 88 tons of NaOH pellets are needed to produce 8000 tons of biodiesel using NaOH

Table 21.2 Immobilization of hydrolytic enzymes on nanomaterials for biofuel process

Nanomaterials	Immobilized enzymes	Immobilization efficiency	Catalytic efficiency after reuse	Reference
Carbodiimide-activated MWCNTs	Cellulase	85%	75% after 6 cycles	Ahmad and Khare (2018)
Chitosan-coated MNPs	Cellulase	–	51.5% after 3 cycles	Javid et al. (2022)
	Cellulase	100%	80% after 15 cycles	Sanchez-Ramirez et al. (2017)
Magnetic iron NPs	β-Glucosidase	89.78%	85% after 10 cycles	Chamoli et al. (2020)
Fe_2O_3 NPs	Laccase	–	50% after 6 cycles	Gou et al. (2020)
MnO_2 NPs	Cellulase	75%	–	Cherian et al. (2015)
Ni NPs	Cellulase	93%	84% after 10 cycles	Rashid et al. (2022)
Mesoporous silica NPs	Xylanase	90%	80% after 9 cycles	Ariaeenejad et al. (2020)
	β-Glucosidase	100%	70% after 7 cycles	Sannino et al. (2020)
		82%	83% after 9 cycles	Pota et al. (2022)
Ag NPs	Cellulase	–	73% after 6 cycles	Mishra and Sardar (2015)
TiO_2-lignin hybrid support	Cellulase	80%	90% after 10 cycles	Zdarta et al. (2017)
Zinc ferrite NPs	Cellulase	88%	50% after 5 cycles	Manasa et al. (2017)

as homogeneous catalyst, whereas only 5.6 tons of supported MgO are required for production of the same amount of biodiesel using MgO as heterogeneous catalyst. Another study developed and applied a heterogeneous CaO/Ag nanocatalyst to the production of biodiesel from soybean oil (Zhu et al. 2021). It was reported that a 5% loading of CaO/Ag yielded 91% biodiesel yield, while 88% was yielded for CaO-catalyzed transesterification at same reaction conditions. Recently, a techno-economic study of a 21 million kg/year biodiesel plant was conducted by Naveen Kumar and Baskar (2020). The biodiesel revenue was reported 15,224,000 dollars/year with a payback period of 1.15 years.

Carbon nanotubes (CNTs) are allotropes of carbon, which exhibit unique structural, thermal, and biocompatible properties to sustain biofuel production. Since CNTs have a large surface area, they have high loading capacity and less diffusion resistance, making them a prominent nanomaterial for immobilization of enzyme (Yan et al. 2015; Muhulet et al. 2018). According to recent reports, conjugation of enzymes with CNTs also increases their catalytic stability and activity. Ahmad and

Khare (2018) synthesized functionalized multiwalled carbon nanotubes (MWCNTs) via carbodiimide coupling. The application of such bionanoconjugates retained 85% activity with improved pH and thermal stability. Similarly, Na_2O-impregnated-CNT nanocatalysts yielded above 97% of FAME yield (Ibrahim et al. 2020).

The ability of CNTs to carry redox reactions and electron transfer kinetics has led to their use in biosensors and microbial fuel cells (Mohideen et al. 2020). Recently, Shaalan et al. (2022) developed defective MWCNTs with porous and crystalline structures and investigated their gas sensing properties. The fabricated sensor showed the highest response of 8.8% toward ethanol compared to NO, NO_2, CO, and acetone at 30 °C of 50 ppm. Additionally, the present sensor displays exceptional signal repeatability at much lower concentrations and temperatures, resulting in greater reliability and lower power consumption.

21.4 Nanotechnological Applications in Biofuel Production from Agro-Wastes

In recent years, nanotechnology has made breakthroughs in the production of biofuels, revealing the potential of agro-waste as a renewable energy source. The purpose of this section is to review recent development to improve biofuel production from agro-wastes using nano-scale materials. The categories of biofuels that will be considered are biodiesel, biohydrogen, bioethanol, and biogas.

21.4.1 Biodiesel Production

Biodiesel is a promising renewable fuel that emits fewer pollutants, is eco-friendly (highly biodegradable), and can be produced with both edible and nonedible oils. Besides this, animal fat is also considered a good biodiesel feedstock because of its abundance and low cost (Gebremariam and Marchetti 2018).

Recent advances in nanotechnology have made it possible to achieve high yields of biodiesel with applications of nanomaterial (Zuliani et al. 2018; Bano et al. 2020; Ingle et al. 2020a). The incorporation of nanocatalysts improves the catalytic efficiency during transesterification of agro-waste feedstock. Recently, Mohamed and El-Faramawy (2021) evaluated the effect of α-Fe_2O_3/AlOOH nanocatalyst in biodiesel production from cotton seed oil. The nanocatalyst exhibited excellent magnetic responsivity and resulted in high yield of 95%. Similarly, Ibrahim et al. (2022) studied the effects of CaO-Fe_2O_3/AC nanocatalysts on biodiesel production from waste cooking oil. Consequently, a maximum biodiesel yield of 98.3% was achieved at a methanol to oil ratio of 18:1. In another study, a novel trimetallic loaded montmorillonite clay nanocatalyst was investigated for synthesis of biodiesel from nonedible *Celastrus paniculatus* seed oil (Munir et al. 2021). Biodiesel yield of

89.42% was achieved under optimal operation conditions of 1:12 oil to methanol ratio, 3.5% of catalyst amount, and 120 °C of reaction temperature for 3 h.

Several recent studies also explored the effects of various nanocatalysts on biodiesel production using animal fats. It has been shown that applications of $CuFe_2O_4$@CaO and CuO nanocatalyst enhance the catalytic efficiency of transesterification of animal fats, resulting in high biodiesel yield (Seffati et al. 2020; Suresh et al. 2021). Recently, CaO–TiO_2 nanocatalysts have also been used to produce biodiesel from dairy scum with a high biodiesel yield (Nabgan et al. 2022). A summary of recently published studies utilizing nanomaterials for biodiesel production is included in Table 21.3.

21.4.2 Biohydrogen Production

Biohydrogen is considered to be the most energy-efficient and cleanest form of biofuel. Its production is mainly carried out by anaerobic bacteria which use a variety of metabolic routes. Generally, biohydrogen is produced by two fermentation methods, namely, dark fermentation and photo fermentation (Gupta et al. 2013).

The enzyme hydrogenase plays a crucial role in the production of biohydrogen, especially during dark fermentation. It has been shown that Ni- and Fe-based NPs improve dark fermentation performance since they are major hydrogenase cofactors (Yang and Wang 2018; Li et al. 2020). A dark fermentative biohydrogen-producing bacterium was also enriched using NPs of other elements. For example, Sun et al. (2021) showed that the incorporation of 400 mg/L $MnFe_2O_4$ NPs improved the substrate utilization efficiency by 40.1% and 131.9% during mesophilic and thermophilic biohydrogen dark fermentation, respectively. Recently, Veeramalini et al. (2022) evaluated the effects of mixed NPs on the production of biohydrogen using effluent collected from brewery processing. Consequently, addition of mixed NPs showed significant yields (96.2%) during dark fermentation.

The major question remains is how NPs contribute to photosynthetic biohydrogen production. Tahir et al. (2021) evaluated the effect of SnO_2 NPs on biohydrogen production from corn stover. It has been reported that at 150 mg/L of NPs, the biohydrogen yield was 49% higher than at 200 mg/L of NPs in the control sample. Similarly, Zhang et al. (2021a, b) demonstrated that the supplementation of nano-TiO_2 significantly attuned the optimal process conditions and the total concentration of intermediate by-products. This led to an enhanced 32.6% hydrogen yield from corn straw.

Furthermore, light saturation also influences fermentation effectiveness and hydrogen yield during photo-fermentation. Recently, Attia et al. (2021) studied the effect of laser photoactivated graphitic carbon nitride nanosheets and Ni NPs on purple non-sulfur bacteria for biohydrogen production from kitchen leftovers. This method improves the bioenvironmental conditions and the biological response of bacteria, increasing biohydrogen yield by 287%. A summary of the use of nanomaterials in biohydrogen production is given in Table 21.4.

Table 21.3 Summary of application of nanotechnology in biodiesel production

Feedstock/ substrate type	Feedstock/ substrate name	Nanomaterials/ nanocatalyst	Operational conditions	Summary	Reference
Agro-industry waste	Cooking oil (waste)	MPANI@Co_3O_4	Temperature, 90 °C; duration, 4 h; methanol to oil ratio, 1:10; and loading, 1:1	Biodiesel yield, 93%	Bahadoran et al. (2022)
		CaO-Fe_2O_3/AC	Temperature, 65 °C; duration, 3 h, methanol to oil ratio, 18:1; and loading, 3 wt%	Biodiesel yield, 98.3%, and reusability of nanocatalyst, six cycles	Ibrahim et al. (2022)
		Magnetic RHC/K_2O 20%/ Ni	Temperature, 65 °C; duration, 2 h; methanol to oil ratio, 12:1, and loading, 4 wt%	Biodiesel yield, 98.2%, and reusability of nanocatalyst, five cycles	Hazmi et al. (2021)
	Cotton seed oil	α-Fe_2O_3/AlOOH	Temperature, 60 °C; duration, 3 h; methanol to oil ratio, 6:1; and loading, 3 wt%	Biodiesel yield, 95%, and high recyclability	Mohamed and El-Faramawy (2021)
		CaO/NiO impregnated with potassium fluoride	Temperature, 60 °C; duration, 4 h; methanol to oil ratio, 1:15; and loading, 5 wt%	Biodiesel yield, 99%, and reusability of nanocatalyst, three cycles	Kaur and Ali (2014)
	Celastrus paniculatus oil	Trimetallic (Ce, Cu, La)-loaded montmorillonite clay	Temperature, 120 °C; duration, 3 h; methanol to oil ratio, 1:12; and loading, 3.5 wt%	Biodiesel yield, 89.42%	Munir et al. (2021)
	Jatropha oil	$CoMgFe_2O_4$ and $MgFe_2O_4$	Temperature, 60 °C; duration, 3 h; methanol to oil ratio, 7:1; and loading, 0.5 wt%	Biodiesel yield, 89.42%	Ita et al. (2018)
	Palm oil	TiO_2 and Fe_2O_3	Temperature, 65 °C; duration, 2 h; and methanol to oil ratio, 1:4	Biodiesel yield, 91.06% and 84.24%	Prabhahar et al. (2021)
		Na^+-doped clinoptilolite	Temperature, 100 °C; duration, 1.25 h; methanol to oil ratio, 12:5:1; and loading, 3 wt%	Biodiesel yield, 98.2%	Abukhadra et al. (2021)

Livestock waste	Chicken fat	AC/$CuFe_2O_4$@CaO	Temperature, 65 °C; duration, 4 h; methanol to oil ratio, 12:1; and loading, 3 wt%	Biodiesel yield, 95.63%	Seffati et al. (2020)
		CaO/$CuFe_2O_4$	Temperature, 70 °C; duration, 4 h; methanol to oil ratio, 15:1; and loading, 3 wt%	Biodiesel yield, 94.52%	Seffati et al. (2019)
	Dairy scum	CaO-TiO_2	Temperature, 70 °C; duration, 4 h; methanol to oil ratio, 1:20; and loading, 3 wt%	Biodiesel yield, 97.2%	Nabgan et al. (2022)
		CaO	Temperature, 58.56 °C; duration, 4 h; methanol to oil ratio, 12.7:1; and loading, 0.87 wt%	Biodiesel yield, 96.52%	Krishnamurthy et al. (2020)
	Pig tallow	CuO	Duration, 0.5 h; methanol to oil ratio, 30:1; and loading, 2.07 wt%	Biodiesel yield, 97.82%	Suresh et al. (2021)

Table 21.4 Summary of application of nanotechnology in biohydrogen production

Feedstock/ substrate	Nanomaterials	Operational conditions	Summary	Reference
Corn stover	SnO_2	Photosynthetic bacteria HAU-M1; loading, 150 mg/L; and duration, 6 h	Biohydrogen yield, 425 mL/L	Tahir et al. (2021)
	Ni^0 NPs	Duration, 1.45 h; pH, 5; S/B, 3.5; and loading, 10 mg/L	Biohydrogen yield, 1.18 mol/mol glucose	Sun et al. (2020)
Cotton stalk	Fe_3O_4 MNPs	*Enterobacter cloacae*, duration, 1.3 h; and loading, 40 mg/L	Biohydrogen yield, 0.37 mol/mol sugar	Zhang et al. (2021a, b)
Dairy wastewater	Polyaniline NPs	Anaerobic sludge and loading, 40 mg/L	Biohydrogen yield, 54.5 mL/g	Hellal et al. (2022)
	$NiFe_2O_4$ NPs	Temperature, 36 °C; loading, 300 mg/L; pH, 6.5; duration, 12–2 h; and	Biohydrogen yield, 241.3 mL	Fahoul et al. (2022)
Paulownia waste	Zn-doped SnO_2 nanocatalysts	8% Zn doping with 150 mg/L	Biohydrogen yield, 335 mL with a rate of 77 mL/h	Tahir et al. (2022)
Palm oil mill effluent	NiO and CoO NPs	Loading. 1 mg/L	Biohydrogen yield, 0.563 L H_2/g removed	Mishra et al. (2018)
Rice straw	$NiCo_2O_4$ NPs	*Bacillus subtilis* PF1 and *Rhodobacter* sp.	Biohydrogen yield, 34.12 mL/L/h	Srivastava et al. (2021a)
	MNPs	*Bacillus* and *Clostridium* and loading, 1.6 g COD/L	Biohydrogen yield, 21.4–60.6 mL/ g COD removed	Tawfik et al. (2019)
Sugarcane bagasse	Fe_3O_4 NPs	Temperature, 45–60 °C; pH, 5–7; duration, 12 h; and loading, 0.5%	Biohydrogen yield, 3427.0 mL/L after 408 h	Srivastava et al. (2021a)
	Fe_3O_4 NPs	Temperature, 30 °C; anaerobic sludge; pH, 5.0; and loading 200 mg/L	Biohydrogen yield, 0.874 mol/mol glucose	Reddy et al. (2017)
Sweet sorghum stove	Chitosan-coated Fe_3O_4-SiO_2-NPs	*Trichoderma asperellum*; pH, 5.95; and duration 5.3 h	Biohydrogen yield, 2.8 mol/mol sugar	Shanmugam et al. (2020)

21.4.3 Bioethanol Production

Bioethanol is a common alternative fuel in the transport sector because of their high octane number, high evaporation enthalpy, and wide range of combustion properties. Its production involves four multifaceted steps, which include pretreatment, enzymatic hydrolysis, fermentation, and ethanol production (Jeevan Kumar et al. 2020; Joshi et al. 2021).

In the last few years, several detailed reviews have been published on nanomaterial applications in bioethanol production processes, particularly on

pretreatment and hydrolysis (Rai et al. 2016, 2019; Chandel et al. 2022). Another vital step in bioethanol production is fermentation, in which sugar monomers (hexose and pentose) are converted to bioethanol by fermenting microorganism. Several studies have shown that immobilizing microorganisms in nano-scale materials can enhance bioethanol yields and fermentation performances (Sanusi et al. 2019; Gupta and Chundawat 2020).

A recent study evaluated the effect of immobilized *Saccharomyces cerevisiae* SS-4 in calcium alginate MNPs (Ca-MNPs) on wheat straw-based bioethanol production (Sarwar et al. 2022). As a result of immobilization in Ca-MNP, *S. cerevisiae* SS-4 cells produced high amounts of ethanol (49.71 g/L), in comparison to immobilization in Ca (45.66 g/L) and free cells (36.52 g/L) at pH 4.5 and 28 °C for 72 h. Through the implementation of a batch anaerobic system and using potato peel waste, Saeed et al. (2022) examined the effects of *S. cerevisiae* immobilization to graphitic carbon nitride nanosheets (g-C_3N_4) on bioethanol production. It was found that the control sample (0.0 ppm of g-C_3N_4), with no nanomaterial produced only 4% of bioethanol while 150 ppm of g-C_3N_4 produced 22.61% of ethanol. In another study, ZnO/g-C_3N_4 nanomaterials, at 150 mg/L, stimulated *S. cerevisiae* to produce 33.2% more bioethanol than any of the other treatments applied (Attia et al. 2022).

21.4.4 Biogas Production

The process of anaerobic digestion of organic matter in an oxygen-free environment produces biogas, which contains methane, CO_2, and small amounts of other gases. Bio-methane, also called renewable natural gas, is produced either by upgrading biogas (removing CO_2 and other contaminants) or through gasifying solid biomass followed by methanation (Adnan et al. 2019). Due to its indistinguishability from natural gas, it can be used in natural gas vehicles without requiring any changes to transmission and distribution infrastructure as well as end user equipment (Madhusudhanan et al. 2020).

Nanomaterials have shown promising results in anaerobic processes, particularly as electron donors/acceptors and cofactors of hydrogenase and ferredoxin enzymes (Romero-Guiza et al. 2016; Samer et al. 2022). The lag phase and time needed to reach peak conversion have been decreased with trace element-based NPs (Co, Fe, Fe_3O_4, and Ni) at different concentrations and particle sizes (Abdelsalam et al. 2017; Sliem et al. 2021). Table 21.5 summarizes all recent advancements in biogas production process using nanomaterials.

In addition to this, a few studies have also investigated the effects of nano-scale materials on microbial communities during anaerobic digestion process. It was found that NPs promote direct electron transfer between archaeal-bacterial species during syntrophic interactions, thereby favoring the proliferation of methanogens (Rotaru et al. 2014; Wang et al. 2016; Zhang and Lu 2016).

Recently, Hijazi et al. (2020) performed a life cycle assessment in order to study the environmental impact of different NPs (Co, Ni, and Fe_3O_4) in biogas production.

Table 21.5 Summary of application of nanotechnology in biogas production

Feedstock/ substrate	Nanoparticle/ nanomaterial	Operational conditions	Summary	Reference
Barley straw	ZnO NPs	Anaerobic digestion and loading, 10 mg/L	Biogas yield, 390.5 mL/g VS	Hassaan et al. (2020)
Cattle manure	Iron oxide NPs	Anaerobic digestion; temperature, 35–37 °C; and loading, 18 mg/L	Biogas yield, 136.74 L/g VS, and methane CH_4, 64.5%	Singh et al. (2022)
Chicken litter	Fe_3O_4 NPs	Anaerobic digestion and loading, 20 mg/L	CH_4 yield, 137.23 mL/g VS	Aguilar-Moreno et al. (2020)
Canola straw	SiO_2	Anaerobic co-digestion; loading, 0.5 mg/L; duration, 30 days	CH_4 yield, 238.6 mL/g VS	Noonari et al. (2022)
Cow dung	Co NPs	Anaerobic digestion and loading, 1–3 mg/L	Biogas yield, 1.43–4.19%	Abdelwahab et al. (2021)
	Nanoferrites (M_2O_4) (M = Fe, Ni, Co)	Anaerobic digestion and size, 3.5–5.7 nm	Biogas yield, 171.9–220.5%	Sliem et al. (2021)
Durum wheat	ZnO NPs	Anaerobic digestion and loading, 10 mg/L	Biogas yield, 422–457 mL/g VS	Hassaan et al. (2021)
Food waste	Urea caped Fe_3O_4	Anaerobic digestion; temperature, 35–37 °C; duration, 50 days; and loading, 75 mg/L	CH_4 yield, 5.386 L	Ali et al. (2022)
Groundnut shell	Fe_3O_4 NPs	Anaerobic digestion; temperature, 35–37 °C; duration, 35 days; and loading, 20 mg/L	Biogas yield, 130.85 mL/g VS CH_4 yield, 100.86 mL/g VS	Olatunji et al. (2022)
Manure and whey	Co_3O_4 NPs	Dry anaerobic co-digestion and loading, 5 mg/L	Biogas yield, 273.43 mL/g VS, and CH_4, 169 mL/g VS	Samer et al. (2022)
Wheat straw	Fe_3O_4 NPs	Anaerobic digestion and TS, 6%	CH_4 yield, 333.14 mL CH_4/g TS	Liu et al. (2021)

Co NPs emit the least greenhouse gases out of all the NPs used. Moreover, Co NPs provided the lowest values for acidification, human toxicity, and eutrophication, while Ni NPs provided the lowest values for resource and ozone layer depletion. Similarly, Ugwu et al. (2022) performed a comparative assessment of biogas production from enhanced anaerobic digestion of agro-industrial wastes with a variety of enhancement options (such as pretreatment, co-digestion and additive supplementation, etc.), biogas utilization, and digestate management. Among all the scenarios analyzed in this assessment, the combined enhancement (co-digestion + PPy/Fe_3O_4 NPs) option exhibited the lowest global warming potential of 0.0053 kg CO_2 eq/MJ.

21.5 Conclusion and Future Prospective

It is clear from the current review that the incorporation of nanotechnology during valorization of agro-waste into biofuel, starting from preprocessing of the raw biomass to other fabrications stages like hydrolysis, fermentation, trans-esterification, gasification, etc., enhanced this considerably. This improvement is primarily due to the distinctive properties of nanomaterials such as their stability, large surface area to volume ratio, high dispersibility, high catalytic activity, specificity, and reusability. The functionalized MNPs are successfully used for enhancement hydrolysis reaction of different agro-wastes using immobilized nanocatalyst. The metal oxides are also being used as nano-additives to enhance the biofuel performance and yield. However, successful commercialization of agro-waste-based biofuels requires the addressing of several technical barriers including synthesizing nano-scale materials that are less expensive, non-toxic, and environment friendly. A pilot-scale study should be conducted to assess the viability of upscaling biofuel production processes using nanomaterials. Experimental and computational studies are also needed to provide a fundamental understanding of some of the mechanisms involved in biofuel production.

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