Green and Sustainable Separation of Natural Products from Agro-Industrial Waste: Challenges, Potentialities, and Perspectives on Emerging Approaches

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Abstract  New generations of biorefinery combine innovative biomass waste resources from different origins, chemical extraction and/or synthesis of biomaterials, biofuels, and bioenergy via green and sustainable processes. From the very beginning, identifying and evaluating all potentially high value-added chemicals that could be removed from available renewable feedstocks requires robust, efficient, selective, reproducible, and benign analytical approaches. With this in mind, green and sustainable separation of natural products from agro-industrial waste is clearly attractive considering both socio-environmental and economic aspects. In this paper, the concepts of green and sustainable separation of natural products will be discussed, highlighting the main studies conducted on this topic over the last 10 years. The principal analytical techniques (such as solvent, microwave, ultrasound, and supercritical treatments), by-products (e.g., citrus, coffee, corn, and sugarcane waste) and target compounds (polyphenols, proteins, essential oils, etc.) will be presented, including the emerging green and sustainable separation approaches towards bioeconomy and circular economy contexts.

Keywords  Green and sustainable extraction · Sustainable separation · Green analytical techniques · Biomass waste · Biorefinery · Bioeconomy and circular economy

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1 Introduction

Currently, it can be observed that global sustainability challenges are all closely interconnected, such as pollution, climate change, biodiversity loss, poverty, energy, and food security. As stated by Liu et al. [1], only holistic and disruptive approaches integrating various components of human and natural systems are effective in identifying and proposing suitable solutions for these challenges, especially those related to research, development, and innovation (RD&I) in interdisciplinary and transdisciplinary studies. To exemplify this systemic view, Fig. 1 illustrates the Earth surface that, based on the “Dymaxion map” (the Fuller Projection Map), shows the planet as a continuum without splitting any continents, seas, and oceans, where cycles are integrated through flows of matter, energy, and information [1, 2]. Here, Brazil, China, the Caribbean, and Africa interact across space, time, and organizational levels in many ways. For instance, the expansion of soybean production aggravates deforestation in Brazil, but also provides food and feedstock to China. The food trade between both countries also affects other areas, including the Caribbean and Africa. Dust particles from the Sahara Desert, also increased due to unbalanced agricultural practices, can reach the Caribbean and have an impact on coral reefs and soil fertility, diminishing tourism in this region. In addition, nutrient-rich particles from Africa can reach Brazil, improving its forest productivity.

According to the Director-General of the Food and Agriculture Organization (FAO) of the United Nations [3], after years of progress, world hunger has increased since 2015. Around 60% of the world’s starving people are from countries affected by conflict and climate change, including northeast Nigeria, Somalia, South Sudan, and Yemen with 20 million people, often suffering extreme climatic events such as droughts and floods. Not surprisingly, some of the FAO’s top priorities for the next

![Fig. 1](image_url)
2 years include topics such as sustainable agriculture, climate change mitigation and adaptation, water scarcity and support of subsistence rural practices, and fisheries and forestry [3, 4]. The challenges related to this demanding context can be intensified and better understood when taking into account that the world population is expected to increase by about 30% over the next 35 years, reaching more than 9.5 billion people in 2050 and 11.2 billion in 2100 [5].

As pointed out by Xia et al. [6], the global food waste of approximately 1.3 billion tons per year is shocking in this context and, although it should be avoided or minimized, it cannot be completely prevented nowadays. Primary and secondary processing generates unpreventable food supply chain waste. This can be due to a number of factors along the supply chain, differing by the commodity and country in question. In general terms, developing countries such as some African countries suffer the greatest loss during the early, upstream part of the primary processing, corresponding to 75% of food losses during production and postharvest. Various initiatives, e.g., building better infrastructure through knowledge transfer (more efficient storage and transport technologies) and improving collaboration and market opportunities in the food supply chain could have a positive role. In industrialized countries, waste occurs especially in the consumption stage, accounting for 50% of overall loss of crops in some countries of North America, Europe, and Oceania. In this case, together with educational and cultural actions, other aspects such as developing legislation to make date labels more user-friendly for consumers (sell-by, best-before, and consume-by), redesigning packaging characteristics (avoiding the “buy 1 get 2” offers) and retailer marketing strategies should be considered [7].

It is estimated that around 140 billion tons of biomass from the agricultural sector are generated every year in the world [8, 9], and a considerable part is recognized as waste and not conflicting with food availability, e.g., leaves, roots, stalks, bark, bagasse, straw residues, seeds, wood and animal residues. Using alternative strategies to avoid additional losses and produce several high value-added chemicals could minimize the volume of non-renewable materials used today (i.e., roughly 50 billion tons of fossil fuels), enough to greatly reduce greenhouse gas emissions and dependence on non-sustainable resources. Therefore, considering their available volume and practically low costs locally and globally, associated to rich function, structure and chemical heterogeneity, all agro-industrial waste should also be considered for their chemical and material potential, as well as a source of energy [10–13].

An important proposal related to waste hierarchy as a framework for residue management can be seen in Fig. 2 [14, 15], which was reformulated to include agro-industrial waste. In this case, the agro-industrial waste hierarchy has a different meaning from top to bottom, since all biomass is valued as raw material. ‘Prevention’ is an intrinsic part of optimized processes, avoiding overproduction. Therefore, the least probable option is ‘disposal’ as the supply chain is designed to attend sustainable consumption, using all bio-based material generated. Here, sustainable production also includes eco-efficiency, cleaner and green productivity, whereas sustainable consumption allows greener choices to be made by individuals based on eco-procurement, supply chain management, waste minimization, recycling, and resource efficiency measures. Both sustainable production and consumption comprises ‘life-cycle thinking’, aiming at preventing problems shifting from one
One of the most important and cited references highlighting the advances in genetics, biotechnology, process chemistry, and engineering that has helped establish a new manufacturing concept to convert renewable biomass into valuable fuels and products, known as biorefinery, was published by Ragauskas and collaborators in the mid-2000s [16]. According to these authors and other researchers [16, 17], integrating biomass and biorefinery technologies has the potential to develop sustainable bio-based energy and materials leading to a new manufacturing paradigm (Fig. 3).

In fact, this paradigm is currently connected to other strong concepts, i.e., bioeconomy and circular economy; the latter is described as an industrial system that is restorative by intention and design. This idea replaces the end-of-life notion with regeneration, focusing on the use of renewable energy, elimination of toxic chemicals, reutilization, return and eradication of “waste through the superior design of materials, products, systems, and business models” [18, 19].

As can be noted, new generations of biorefinery combine innovative biomass resources from different origins, chemical extraction and purification and/or synthesis of biomaterials, biofuels and bioenergy via benign processes. From the very beginning, the identification and quantification of all potentially high value-added
compounds that could be removed from the available renewable feedstocks requires another analytical approach, also connected to green chemistry [20, 21].

2 From Green to Sustainable Separation: Towards Holistic, Flexible, and Zero-Waste Biorefineries

More recently, green extraction and purification have been presented as methods based on establishing processes that reduce energy consumption, using solvents and renewable materials, as well as ensuring a safe and high-quality fraction/product [22]. The aim of their application is to obtain natural products from industrial waste, which is considered a highly attractive initiative [23].

However, a more adequate term for such extraction and purification processes towards vanguard biorefineries could be sustainable separation, adding to the previous green definition, the notion of innovation across all sectors that allows for
increased value in a wide sense, enhancing human and environment benefits and providing economically accessible technologies also advantageous to industry and large scale processing systems. It includes another dimension related to the generation of more creative and healthy jobs, contributing to the construction of a positive long-term sustainability agenda, encompassing bio-circular economy, environmental and social justice [24–27].

Sustainable separation can be defined as a holistic approach grounded on the circular and flexible design and application of renewable benign materials and auxiliaries (including bio-derived solvents, solid phases, membranes) and processes [rooted on green analytical techniques and sustainability metrics and indices, e.g., life cycle analysis (LCA), chemometrics, and other interdisciplinary indicators]. The aim is to optimize the tuneable use of energy, time, reagents, devices, scale, yield and number of steps to extract, fractionate, purify or even modify the components of interest from bio-derived waste during these in situ processes, ensuring analytical reproducibility, efficiency, selectivity robustness and scalability, with online evaluation regarding measurable objectives to create safer, healthier, and more efficient products, processes, and services under fair conditions, commercially available at accessible and just prices [28–30].

Natural products are among the most attractive value-added chemicals to be considered, which can be classified as organic compounds formed by living systems divided into three main categories: (1) compounds that occur in all cells and have a central role in their metabolism and reproduction (nucleic acids, amino acids, and sugars), also known as primary metabolites; (2) high-molecular polymeric materials which form cellular structures (cellulose, lignins, and proteins) and; (3) chemicals which are characteristic of a limited number of species, called secondary metabolites [22, 30]. Many of these bioactive compounds (e.g., alkaloids, terpenoids, and phenols) have been extensively used as medicine, nutraceuticals, flavors, fragrances, cosmetics, food additives, antimicrobials, bio-pesticides, etc. However, among the biggest challenges for biomass utilization is establishing benign methods to separate, purify and modify it into chemicals, fuels, and new materials. This is partially due to, with rare exceptions, the small amounts which are lower than 0.01% of the dry weight of vegetal, associated to possible product inhibition issues, large raw material variability, feed detoxification (when necessary), instability of the target compound (or fractions) and its presence in a complex mixture [23, 30].

It is well known that the separation steps, especially extraction, correspond up to 40–80% of the total costs of most common chemical processes currently used. From the point of view of a holistic biorefinery, separation has attracted more and more attention [31]. For instance, for natural products, solvent-based extraction is one of the best options nowadays considering the nature of many bio-based chemicals and matrices, and also the fact that other separation methods, such as those based on chromatography or membranes, do not have the same advantages taking into account commercial scales [32].

It is expected that high value-added components from biomass waste such as essential oils, polyphenols, and other food or medicinal-related products are extracted first, followed by polysaccharides, lignocelluloses or waxes via advanced separation and depolymerization processes. Among them, green solvents in general,
supercritical CO₂, subcritical water, microwave (MW)-assisted acidolysis and gas-expanded liquids have been mentioned [33]. Green solvents offer important separation advantages, including near-supercritical or supercritical fluids, which have outstanding mass transport properties, polarity, and easiness of solvent removal after extracting the compound of interest [34]. Another interesting solvent is water, but the range of compounds that are soluble in this medium is quite limited. Nevertheless, the use of subcritical water has been demonstrated to be advantageous for organic modification to depolymerize, hydrolyze, gasify, and carbonize biomass to produce bioactive compounds, sugars, biogas, and other valuable solids [16, 35].

Integrating two or more green techniques combining different strategies has played an important role in overcoming the main drawbacks of a single technique towards sustainable separation. For instance, for high-pressure solvent extraction in which the extractants do not reach supercritical conditions, the temperature, time, and solvent consumed can be dramatically reduced associating ultrasound-assisted treatment [28, 36]. In fact, more attention has been paid to green extraction, purification, or modification of natural products derived from agro-industrial waste nowadays, opening up new opportunities for sustainable approaches designed for bioeconomy and circular economy models. The aim of this paper is to present an overview of the design and application of green and sustainable separation of natural products for vanguard zero-waste biorefineries. The main analytical techniques and procedures described over the last 10 years will be described in detail, showing the potentialities, challenges, and perspectives in this topical and emergent scenario.

3 High Value-Added Approaches for Green and Sustainable Separation of Natural Products from Waste: What can be Observed from the Literature?

More recently, trends in green and sustainable extraction, fractionation and purification techniques have largely focused on minimizing the use of solvents, energy and materials that are intrinsically benign to human health and the environment [37]. In order to analyze the status quo and perspectives related to natural product separation from waste, a systematic literature review was conducted using the ISIS Web of Knowledge platform (reviews and papers) from 2006 to 2017, combining the descriptors “natural product” and “green extraction/separation” (or “sustainable extraction/separation”) and “waste” (or “residue”). Figure 4 shows the number of publications during this period. There were more than 160 research papers and reviews that, to the best of our knowledge, are reasonably representative to show the strongest tendencies in this field over the last decade. It can be clearly observed that there has been an increase in the number of manuscripts over the last 10 years, covering the principles, advances, and applications of these green methods.

The obtained data reflect the growing interest and potential of green and sustainable methods to separate natural products from waste. One tendency observed in particular was the innovative ways to remove (integrating extraction, purification and/or modification in the same integrated system) and use such compounds in more
contemporary sectors, promoting human and environmental health instead of general and old-fashioned remediation [19, 38]. As a result, new applications for food, nutraceutical, and agricultural sectors have been further explored, based on their advantageous properties as natural colorants, flavors, aromas, antioxidants, antifungals, bioformulations (bio-pesticides) or simply their use as precursors to generate other compounds for similar uses. Some details related to patents, (non-) clinical trials, sustainable indicators, scaling-up, regulatory, agro-industrial variability and availability, traceability, seasonality, good laboratory and manufacturing practices, additional economical and marketing issues have also been discussed.

Table 1 presents the research papers and reviews published during this period, highlighting their main focus, the green or sustainable techniques/approaches adopted, raw materials (mostly agro-industrial waste) and target compounds studied. The most common raw materials described as chemical feedstocks were waste derived from plants, for instance, food, mainly fruits (citrus, mango, papaya, grape, passiflora, banana, tomato, olive), grains (corn, soybean, sunflower, coffee) and other abundant materials (sugarcane bagasse, tea, wood bark, rice and wheat straw). Additional issues that affect the quality of the final products were also discussed, namely the procedure used for waste collection, selection, storage, drying, matrix characteristics (particle size, shape, specific surface area and porosity). The latter aspects play an important role in extraction efficiency due to the mass and heat transfer processes. Understanding the nature of raw material is crucial to avoid negative influences impacting the quality and yield during the removal of the target compounds, e.g., caused by co-extracted contaminants or due to the presence of some
| Year | Crop                  | Waste stream      | Target compounds                  | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|-----------------------|-------------------|-----------------------------------|-----------------------|----------------------------------------------------------------------------------------------------------------|------------|
| 2017 | Olives                | Olive kernels     | Phenolic compounds and oil        | France and Spain       | Aqueous liquid solid extraction (LSE), mechanical expression (ME), supercritical CO₂ (SC-CO₂) and gas-assisted mechanical expression (GAME) | Gas-assisted mechanical expression (GAME) for the selective recovery of lipophilic and hydrophilic compounds from olive kernel [145] |
| 2017 | Figs                  | Leaves            | Bioactive compounds               | China                 | Deep eutectic solvent with microwave and ultrasound extraction Time: 10 min (MW) and 60 min (US) Temperature: 40–80 °C Power: 250 W (MW) and 700 W (US) | Enhanced and green extraction polyphenols and furanocoumarins from Fig (Ficus carica L.) leaves using deep eutectic solvents [136] |
| 2017 | *Polygonum multiflorum* | Herbal raw materials | Stilbene glycoside and anthraquinones | China                 | Ionic liquids with ultrasonic extractor Time: 1–120 min Power: 40–120 W | Sequential extraction and separation using ionic liquids for stilbene glycoside and anthraquinones in *Polygonum multiflorum* [131] |
| 2017 | Several sources       | Not defined       | Mostly bioactive compounds         | Spain                 | Review Critical overview about the greenness of water as extraction solvent | Water as green extraction solvent: Principles and reasons for its use [146] |
| 2017 | Pomelo                | Flavedo           | Essential oil                     | China                 | Microwave irradiation Power: 240–700 W Time: 24 min | A process to preserve valuable compounds and acquire essential oils from pomelo flavedo using a microwave irradiation treatment [52] |
| 2017 | *Selaginella doederleinitii* | Not defined | Biflavonoids                      | China                 | Ionic liquids and microwave-assisted extraction Power: 300–700 W Time: 30–50 min Temperature: 40–60 °C | Optimization of ionic liquid-assisted extraction of biflavonoids from *Selaginella doederleinitii* and evaluation of its antioxidant and antitumor activity [132] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2017 | *Pogostemon cablin* | Leaves | Essential oils | Indonesia | Microwave-assisted hydrodistillation (MAHD) and solvent-free microwave extraction (SFME) Power: 600 W (MAHD) and 264 W (SFME) Time: 66 min (MAHD) and 45 min (SFME); solvent: water | Comparison of conventional and microwave-assisted distillation of essential oil from *Pogostemon cablin* leaves: analysis and modeling of heat and mass transfer [147] |
| 2017 | *Juglans regia* L. | Fresh male flowers and unripe walnut seeds | Phenolic content and water-soluble polyphenols | Italy | Microwave-assisted extraction Frequency: 2.45 GHz Max. power: 500 W Solvent: ethanol/water Temperature: 60–100 °C Time: 6–30 min | Process intensification by experimental design application to microwave-assisted extraction of phenolic compounds from *Juglans regia* L. [148] |
| 2017 | Walnuts | Walnut de-pellicle | Flavonoids | China | Macroporous resins Pretreated with 5% HCl and 5% NaOH solutions | Recovery of flavonoids from walnuts de-pellicle wastewater with macroporous resins and evaluation of antioxidant activities in vitro [149] |
| 2017 | Ginseng | Roots | Bioactive compounds | Brazil | Sequential extraction system using ethanol followed by water Temperature: 333 K Time: 5–240 min | Techno-economic evaluation of obtaining Brazilian ginseng extracts in potential production scenarios [150] |
| 2017 | Food ingredients and natural products | Not defined | Nutraceuticals, cosmetic, pharmaceutical, and bioenergy applications | France | Review current knowledge on ultrasound-assisted extraction | Ultrasound-assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review [151] |
| Year | Crop                          | Waste stream               | Target compounds                        | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|-------------------------------|----------------------------|----------------------------------------|-----------------------|-----------------------------------------------------------------------------------------------------------|------------|
| 2017 | Coffee                        | Coffee chaff               | Antioxidants                           | Portugal             | Solid–liquid extraction and multi-frequency multimode modulated (MMM) Frequency: 19.8 kHz Power: 250 and 500 W Time: 60–600 s Multi-frequency multimode modulated technology as a clean, fast, and sustainable process to recover antioxidants from a coffee by-product [152] |           |
| 2017 | Apples                        | Wild apple fruit dust      | Bioactive compounds, polyphenolic antioxidants | Serbia               | Microwave-assisted extraction Time: 15–35 min Ethanol conc.: 40–80% Irradiation power: 400–800 W Microwave-assisted extraction of wild apple fruit dust production of polyphenol-rich extracts from filter tea factory by-products [153] |           |
| 2017 | Wood                          | Wood biomass               | Lignin oligomers                        | China                | Microwave-assisted treatment with deep eutectic solvent Solvent: choline chloride and oxalic acid dehydrate Temperature: 80 °C Power: 800 W Time: 3 min Efficient cleavage of lignin-carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent [137] |           |
| 2017 | Wood                          | Oak wood from cooper-age by-products | Furanic compounds, cis- and trans- B-methyl-y-octa-lactones, terpenes and norisoprenoids, benzenic compounds | Spain                | Pressurized liquid extraction Solvent: water, ethanol/water (80:20) and ethyl lactate Temperature: 60–120 °C Pressure: 10.34 MPa Flush volume: 60% Puriing time: 80 s Extraction of natural flavorings with antioxidant capacity from cooper-age by-products by green extraction procedure with subcritical fluids [154] |           |
| 2017 | P. armeniaca, P. persica, P. domestica, Triticum aestivum | Fruit and vegetables seeds and peels | Phenolic compounds                      | Pakistan             | Ultrasonic water bath Solvent: 65% (v/v) ethanol (methanol and acetone) Extraction time: 30 min Temperature: 50 °C Extraction and quantification of phenolic compounds from *Prunus armeniaca* seed and their role in biotransformation of xenobiotic compounds [71] |           |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2017 | Lignocellulose materials | Lignocellulosic biomass such as crops or forestry residues | High value-added bio-based products (e.g., bioethanol, biogas, acetic acid, acetic acid, or activated carbon) | Mexico and Pakistan | Review Focus on transformation based on syngas platform (thermochemical platform) and sugar platform (biochemical platform) | Lignocellulose: a sustainable material to produce value-added products with zero-waste approach [155] |
| 2017 | Olives | Olive by-product (paté) | Fatty acids and phenolic compounds | Spain and Italy | Soxhlet extraction (percolation with petroleum ether, under reflux) | Macro and micro functional components of a spreadable olive by-product (pate) generated by new concept of two-phase decanter [156] |
| 2017 | Tucumá palm fruit | Tucumá’s endocarp | Cellulose | Brazil and USA | Alkaline extraction (135 °C, autoclave, 2 bar, 2 min, 20% of aqueous NaOH, 1:30 straw to liquor (g/ml), 30 min) | New approach for extraction of cellulose from tucumá’s endocarp and its structural characterization [115] |
| 2017 | Grapes | Seeds | Resveratrol | China | Subcritical water extraction Pressure: 0.5–1.5 MPa Time: 20–30 min Temperature: 130–170 °C | Optimization of subcritical water extraction of resveratrol from grape seeds by response surface methodology [100] |
| 2017 | Mango, rambutan, santol | Peels | Antioxidant activity | Thailand | Solid–liquid extraction Ethanol (95%) | Study effect of natural extracts on the antioxidant activity in pork balls [157] |
| 2017 | Tomatoes | Pericarps without seeds | Nutrient-rich antioxidant ingredients | Portugal, Spain, Ireland | Microwave extraction (600 rpm, 200 W) Time: 0–20 min Temperature: 60–180 °C Ethanol conc.: 0–100% Solid/liquid ratio: 5–45 g/l | Valorization of tomato wastes for development of nutrient-rich antioxidant ingredients: a sustainable approach towards the needs of today’s society [158] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|-----------------------|------------------------------------------|------------|
| 2017 | Citrus latifolia, Rubus sp., Origanum vulgare and Heterotheca inuloides | Peel and broken down vegetable material | Fatty acids and antioxidants compounds | Mexico, Belgium | SC-CO₂ Extraction time: 1 h Flow: 25 g/min Pressure: 10–40 MPa Temperature: 35–60 °C Co-sol.: 0–8 g/min Percent flow: 0–32% | Thermodynamics and statistical correlation between supercritical CO₂ fluid extraction and bioactivity profile of locally available Mexican plant extracts [159] |
| 2017 | Pomegranates | Peels | Carotenoids | Greece | Ultrasound-assisted extraction (139 W, 20 kHz); solvents: vegetable oils Extraction time: 10–60 min Temperature: 20–60 °C | Green ultrasound-assisted extraction of carotenoids from pomegranate wastes using vegetable oils [72] |
| 2017 | Pomegranates | Both edible and non-edible parts | Polyphenols | Greece | Semi-automatic extractor Solvents: H₂O, β-CD, HP-β-CD Extraction time: 363 min Temperature: 25 °C | Green extraction of polyphenols from whole pomegranate fruit using cyclodextrins [121] |
| 2016 | Quince | Leaves | Natural dyes and bioactive compounds | Romania | Aqueous extraction Extraction time: 60–240 min Temperature: 4–100 °C | Dyeing and antibacterial properties of aqueous extracts from quince (Cydonia oblonga) leaves [160] |
| 2016 | Corn | Steep liquor | Vanillic acid, p-coumaric acid, ferulic acid, sinapic acid and quercetin | Spain, Portugal, and Italy | Liquid-liquid extraction Solvents: chloroform (56 °C, 60 min) Ethyl acetate (25 °C, 45 min) | A multifunctional extract from corn steep liquor: antioxidant and surfactant activities [161] |
| 2016 | Palm | Oil palm empty fruit bunches | Cellulose with polypropylene as biocomposite material | Malaysia, Pakistan | Ultrasound treatment (40 kHz) solvent: hydrogen peroxide Extraction time: 1–3 h Room temperature | Autoclave and ultra-sonication treatments of oil palm empty fruit bunch fibers for cellulose extraction and its polypropylene composite properties [73] |
| 2016 | Tomatoes | Seeds and peels | Carotenoids/proteins | Tunisia and Germany | Supercritical CO₂ extraction 80 °C, 400 bar, 4 g CO₂/min for 2 h | Biorefinery cascade processing for creating added value on tomato industrial by-products from Tunisia [82] |
| Year | Crop     | Waste stream                  | Target compounds                              | Geographical location | Green or sustainable separation approach | References                                                                 |
|------|----------|-------------------------------|-----------------------------------------------|-----------------------|------------------------------------------|---------------------------------------------------------------------------|
| 2016 | Black tea| Black tea processing waste    | Antioxidant and antimicrobial phenolic compounds | Turkey and USA        | Solvent extraction                       | Black tea processing waste as a source of antioxidant and antimicrobial phenolic compounds [46] |
| 2016 | Rapeseed | Rapeseed oil cakes            | Protein- and lignin-rich fractions            | France                | Ultrafine milling and electrostatic separation | Chemical- and solvent-free mechano-physical fractionation of biomass induced by tribo-electrostatic charging: separation of proteins and lignin [139] |
| 2016 | Sunflower| Seeds                         | Sunflower protein-based ingredients           | USA                   | Review                                    | Chlorogenic acid oxidation and its reaction with sunflower proteins to form green-colored complexes [162] |
| 2016 | Passion fruit| Peels                    | Pectin                                       | Malaysia              | Acidic and enzymatic extraction          | Comparison of acidic and enzymatic pectin extraction from passion fruit peels and its gel properties [107] |
| 2016 | Red grape| Pomace                        | Polyphenols and anthocyanin pigments         | Greece                | Ultrasound-assisted extraction           | Development of a green process for the preparation of antioxidant and pigment-enriched extracts from winery solid wastes using response surface methodology and kinetics [74] |
| Year | Crop                        | Waste stream                  | Target compounds               | Geographical location | Green or sustainable separation approach | References                                                                 |
|------|-----------------------------|-------------------------------|--------------------------------|-----------------------|------------------------------------------|-----------------------------------------------------------------------------|
| 2016 | Orange and lemon            | Fresh and waste peel          | Pectin and α-limonene         | Portugal and Italy    | Microwave, Solvent: water, Extraction time: 1 h, Temperature: 80 °C | Eco-friendly extraction of pectin and essential oils from orange and lemon peels [53] |
| 2016 | Coffee                      | Spent coffee grounds          | Oil                            | China                 | Ultrasonication extraction, Solvent: hexane, Extraction time: 15–75 min | Effect of oil extraction on properties of spent coffee grounds-plastic composites [98] |
| 2016 | Tomato                      | Waste of tomato paste plants  | Lycopene                       | Iran and Canada       | Microemulsion technique (MET), Solvents: water, saponin: glycerol, surfactant: lycopene, Extraction time: 30 min, Temperature: 25 °C | Enhanced lycopene extraction from tomato industrial waste using microemulsion technique: optimization of enzymatic and ultrasound pre-treatments [163] |
| 2016 | Red capsicum (*Capsicum annuum*) | Processing residue           | Carotenoids                    | India                 | Enzymatic liquefaction, Pectinase, viscozyme L, cellulose extraction, Time: 1 h, Temperature: 60 °C | Enzyme-assisted extraction of carotenoid-rich extract from red capsicum (*Capsicum annuum*) [108] |
| 2016 | Rice                        | Husk                          | Cellulose                      | India                 | Eco-friendly method, montmorillonite, LiOH, H₂O₂, Extraction time: 6 h, Temperature: 80 °C | Extraction of cellulose from agricultural waste using montmorillonite K-10/LiOH and its conversion to renewable energy: biofuel by using *Myrothecium gramineum* [122] |
| 2016 | Tea (yarrow and rose hip)   | By-products from filter-tea factory | Chlorophylls and carotenoids | Serbia                | Supercritical fluid extraction, Extraction time: 5 h, Temperature: 40 and 60 °C, Pressure: 100–300 bar, CO₂ flow rate: 0.194 hℓ/ℓ | Extraction of minor compounds (chlorophylls and carotenoids) from yarrow-rose hip mixtures by traditional versus green technique [83] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2016 | Corn, sugarcane, sorghum, pearl millet, green gram, groundnut sesame | Bagasse, stover, stalk and shell | Para-coumaric acid (pCA) | India and USA | Alkaline hydrolysis pH 3, alkali conc.: 0.5–4 M | Extraction of p-coumaric acid from agricultural residues and separation using 'sugaring out' [116] |
| 2016 | Winery | Grape wastes and by-products | Antioxidant compounds and polyphenols | Denmark, China, France and Brazil | Review | Green alternative methods for the extraction of antioxidant bioactive compounds from winery wastes and by-products: a review [164] |
| 2016 | 1st to 3rd generation biodiesel feedstocks | Mostly microalgae | Biodiesel | Malaysia and Japan | Review | Green biodiesel production: a review on feedstock, catalyst, monolithic reactor, and supercritical fluid technology [84] |
| 2016 | Jatropha curcas, oil palm | Seeds, empty fruit bunch | Bio-oil | Malaysia | Microwave extraction Solvent: water Extraction time: 60–140 min Power: 200–700 W | Green bio-oil extraction for oil crops [54] |
| 2016 | Green tea | Green tea residue | Protein | The Netherlands | Alkaline protein extraction Solvent: NaOH Extraction time: 2 h Temperature: 95 °C | Improving yield and composition of protein concentrates from green tea residue in an agri-food supply chain: effect of pre-treatment [117] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2016 | Eucalyptus wood | Eucalyptus chips | Hemicelluloses | Uruguay | Green liquor extraction Solvents: water and green liquor (Na₂CO₃, Na₂S, and NaOH) extraction time: 30–150 min temperature: 100–160 °C | Integrated forest biorefineries: green liquor extraction in eucalyptus wood prior to kraft pulping [123] |
| 2016 | Watermelons | Juice | Lycopene | Brazil | Microfiltration, dialfiltration, reverse osmosis α-Al₂O₃ membranes T1-70 (35 °C) Polyamide composite membranes (35 °C, 60 bar) | Integrated membrane separation processes aiming to concentrate and purify lycopene from watermelon juice [140] |
| 2016 | Larch wood | Sapwood, heartwood, bark and branches | Phenolic compounds | Slovenia | Pressurized hot water Extraction time: 30 min Temperature: 100 °C | Isolation of phenolic compounds from larch wood waste using pressurized hot water: extraction, analysis and economic evaluation [165] |
| 2016 | Tomatoes | Pomace | Lycopene | Iran | Microemulsion technique H₂O and surfactants Extraction time: 30 min Temperature: 35 °C | Microemulsion-based lycopene extraction: effect of surfactants, co-surfactants, and pretreatments [166] |
| 2016 | Melons | Rind | Carbohydrates, phenolic compounds, and fatty acids | Spain | Solvent extraction Solvent: cyclohexane, ethanol Extraction time: 2 h Microwave radiation: 190 °C, 20 min, 200 W | Microwave heating for the catalytic conversion of melon rind waste into biofuel precursors [167] |
| 2016 | Tomatoes, fungus *Blakeslea trispora* | Processing waste | Lycopene | Greece | Review Emphasis on final product safety and eco-friendly processing (solvent extraction, SFE, MAE, high-pressure processing, ultrasound, electrical methods) | Natural origin lycopene and its "green" downstream processing [168] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2016 | Oranges | Peel | Pectin | Italy | Conventional hydrodistillation, MAE, US Solvents: water Extraction time: 5–155 min Temperature: 90–333 °C | Novel configurations for a citrus waste based biorefinery: from solventless to simultaneous ultrasound and microwave-assisted extraction [55] |
| 2016 | Lemons, olives, onion, red grape, coffee, and wheat | Peel, leaves, solid wastes, pomace, spent filter and bran | Polyphenolic compounds | Greece | Ultrasound extraction (140 W, 37 kHz) eutectic mixtures Extraction time: 90 min Temperature: 80 °C | Novel glycerol-based natural eutectic mixtures and their efficiency in the ultrasound-assisted extraction of antioxidant polyphenols from agri-food waste biomass [75] |
| 2016 | Potatoes | Peels | Polyphenolic antioxidants | Greece | Ultrasound extraction (140 W, 37 kHz) Solvents: ethanol and glycerol Extraction time: 90 min Extraction temperature: 50–80 °C | Optimization of a green ultrasound-assisted extraction process for potato peel (Solanum tuberosum) polyphenols using bio-solvents and response surface methodology [76] |
| 2016 | Grapes | Seeds | Grape seed oil | Croatia | Supercritical CO₂ Extraction time: 90 min Temperature: 35–64 °C Pressure: 158–441 bar CO₂ flow rate: 1.94 kg/h | Optimization of supercritical CO₂ extraction of grape seed oil using response surface methodology [85] |
| 2016 | Crocus sativus | Petals (underutilized bulk agro-waste) | Phenolic compounds | Iran | Subcrirical water extraction Extraction time: 20–60 min Temperature: 120–160 °C | Optimization of the subcritical water extraction of phenolic antioxidants from Crocus sativus petals of saffron industry residues: Box–Behnken design and principal component analysis [101] |
| 2016 | Bananas | Peels | Antioxidants | Malaysia and Turkey | Solvent extraction Solvents: acetone, ethanol, hexane, methanol, H₂O Extraction time: 1–5 h | Optimization of extraction parameters on the antioxidant properties of banana waste [47] |
Table 1 (continued)

| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|-------------------|-----------------------|------------------------------------------|------------|
| 2016 | Pea vine | Pea vine waste | Potential platform molecules (5-hydroxy furfural; ethanoic acid); sugars (levoglucosenone, rhamnose, xylose, fructose); biopolymer with pectinaceous and starch-like characteristics | United Kingdom | Pseudo-subcritical water extraction Temperature: 125–175 °C Pressure: 20–60 bar Flow rate: 1–5 ml/min | Potential utilization of unavoidable food supply chain wastes valorization of pea vine wastes [6] |
| 2016 | Keratin-containing products stored in large waste deposits | Processing waste | Keratin | Romania | Review Keratins solubilization (protected and unprotected methods) followed by dehydro-thermal, physical-type bonding or chemical treatments | Practical ways of extracting keratin from keratinous wastes and by-products: a review [169] |
| 2016 | *Taxus baccata* L. | Case study based on European yew | 10-deacetyl baccatin III (10-DAB) | Germany | Review Theoretical approach in thermodynamics and process modelling as an alternative process design | Process design for integration of extraction, purification and formulation with alternative solvent concepts [170] |
| 2016 | Olives | Olive mill waste water | Biophenols (hydroxytyrosol and tyrosol) | Italy | Liquid-liquid extraction Solvents: *n*-hexane, EtOAc | Quick assessment of the economic value of olive mill waste water [171] |
| 2016 | Olives | Olive mill waste water | Tyrosol | Spain, United Kingdom and Spain | Hydrophobic ionic liquids Solvents: ILs Extraction time: 2 h Temperature: 303–323 K | Recovery of tyrosol from aqueous streams using hydrophobic ionic liquids: a first step towards developing sustainable processes for olive mill wastewater (OMW) management [133] |
| 2016 | Cupuassu Seeds | Cupuassu butter (phenolic content/tocopherols/fatty acids) | Brazil | Supercritical CO₂ extraction Temperature: 50 and 70 °C Pressures: 20–40 MPa | Supercritical CO₂ extraction of cupuassu butter from defatted seed residue: experimental data, mathematical modeling and cost of manufacturing [86] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|-----------------------|------------------------------------------|------------|
| 2016 | Coffee | Spent coffee grounds | Oil fraction | Portugal, Brazil, Portugal | Supercritical CO$_2$ Extraction time: 1 h Temperature: 55 °C Pressure: 250 bar Flow rate: 15 kg/h | The green generation of sunscreens: using coffee industrial sub-products [87] |
| 2016 | Ginger | Not defined | Essential oil, phenolics, fibers and phenolic acids | France | Microwave hydrodiffusion and gravity processing (MHG) and UAE Solvents: water Extraction time: 83 and 90 min Temperature: up to 100 and 50 °C | Towards a “dry” bio-refinery without solvents or added water using microwaves and ultrasound for total valorization of fruit and vegetable by-products [56] |
| 2016 | Passion fruit | Passion fruit seeds and passion fruit seed cake (the residue from the seed oil production by cold pressing) | Oil and extract with promising antioxidant and antimicrobial activities | Brazil and USA | SFE, LPE, MAC, UE Solvents: sCO$_2$, hexane, ethyl acetate, ethanol, H$_2$O Extraction time: 45 min–7 days temperature: room temp.– 50 °C | Valorization of passion fruit (Passiflora edulis sp.) by-products: sustainable recovery and biological activities [88] |
| 2016 | Wood | Broken pallets, crates, and waste timber from building and demolition works | Renewable energy source | Romania | Review Overview of the technical and economic opportunity of using wood waste as a renewable energy source | Wood waste as a renewable source of energy [172] |
| 2015 | Plants of spontaneous flora, cultivated plant, and wastes resulted in agricultural and food industry | General bio-derived materials | Polyphenols | Romania | Review Microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), and ultrasound-assisted extraction (UAE) | A comparative analysis of the ‘green’ techniques applied for polyphenols extraction from bioresources [173] |
| Year | Crop                  | Waste stream                               | Target compounds                                      | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|-----------------------|--------------------------------------------|------------------------------------------------------|-----------------------|-----------------------------------------------------------------------------------------------------------|-------------|
| 2015 | Onion                 | Onion solid wastes                        | Polyphenol- and pigment-enriched extracts with antioxidant activity | Greece                | Ultrasound extraction (140 W, 37 kHz) Extraction time: 60 min Temperature: 45 °C                          | [174]       |
| 2015 | Six types of plant fibers (bast, leaf, seed, straw, grass, and wood) and animal fibers and regenerated cellulose fibers | Seed (coir) and animals (chicken feather) as they are secondary or made from waste products | Fibers                | Sweden                                                                 | Review Dew, stand, cold and warm water, steam, enzyme, mechanical, ultrasound chemical and Surfactant retting | [175]       |
| 2015 | Non edible vegetables | Seeds                                      | Biodiesel                                            | Egypt                 | Review                                                                                                   | [102]       |
| 2015 | Neem                  | Neem seed cake (NSC)                       | Neem Protein (NP)                                    | USA                   | Alkaline extraction Solvents: H₂O and NaOH Extraction time: 60 min Temperature: 75 °C                  | [118]       |
| 2015 | Oranges               | Peel                                       | Essential oil, polyphenols and pectin               | Algeria and France    | Solvents: “in situ” water Extraction time: 25 and 3 min Temperature: 59 °C                              | [57]        |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|-----------------------------------------|------------|
| 2015 | Corn, sugarcane, sorghum, soybean, rice, barley, potato, other lignocellulose, vegetable oils, oilseed | By-products (bagasse, straw, cobs, stalks, stover, grass etc.) | Biofuel, 1,3-propanediol, succinic acid, adhesives, solvents, surfactants, ethyl lactate, erucic acid, amyllose ethers, among others | Denmark | Review Focus on integrating sustainability assessment procedures and tools (LCA and evaluation approaches) | Biorefining in the prevailing energy and materials crisis: a review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies [144] |
| 2015 | Agro-industrial products | Agro-industrial co-products | Phenolic compounds | Brazil | Solid-state fermentation, even as friendly enzyme-assisted extractions | Biotransformation and bioconversion of phenolic compounds obtainment: an overview [176] |
| 2015 | Cashew-nut | Husk | Natural dyes | India | Enzyme-assisted extraction cellulase and pectinase Solvent: water Extraction time: 60–180 min pH 9.5 | Cashew-nut husk natural dye extraction using Taguchi optimization: green chemistry approach [109] |
| 2015 | Beet | Sugar beet pulp | Monosaccharides present in hydrolyzed SBP pectin: l-rhamnose, l-arabinose, D-galactose and D-galacturonic acid | United Kingdom | Centrifugal partition chromatography ascending mode, 1000 rpm Mobile phase flow rate: 8 ml/min | Centrifugal partition chromatography in a biorefinery context: separation of monosaccharides from hydrolyzed sugar beet pulp [141] |
| 2015 | Mangoes (Mangifera indica L.) and rye grains (Secale cereals L.) | Peels and grains | Alk(en)ylresorcinols (ARs) | Germany | Ultrasound-assisted extraction Solvent: dichloromethane Extraction time: 15 s cooled in ice bath | Development and validation of an HPLC method for the determination of alk(en)ylresorcinols using rapid ultrasound-assisted extraction of mango peels and rye grains [78] |
Table 1 (continued)

| Year | Crop       | Waste stream                                | Target compounds                                                                 | Geographical location                   | Green or sustainable separation approach                                                                 | References |
|------|------------|---------------------------------------------|---------------------------------------------------------------------------------|----------------------------------------|------------------------------------------------------------------------------------------------------------|------------|
| 2015 | Olives     | Waste from olive oil production             | High-added value compounds (polyphenols, fatty acids, coloring pigments (chlorophylls and carotenoids), tocopherols, phytosterols, squalene, volatile and aromatic compounds) | Spain, France, Morocco and Portugal     | Review Conventional (solvent, heat, grinding) and non-conventional methodologies (ultrasounds, microwaves, sub- and supercritical fluid extractions, pressurized liquid extraction, pulsed electric fields and high voltage electrical discharges) | [142]      |
| 2015 | Asparagus  | Dried segments (residues)                   | Antioxidant compounds                                                           | China                                  | Solid–liquid extraction Solvents: acetone, methanol or ethanol Extraction time: 2 h Temperature: 70 ºC | [177]      |
| 2015 | Grapes     | Skin                                        | Anthocyanins                                                                   | Korea                                  | Deep eutectic solvents (DESs) Extraction time: 45 min room temperature                              | [138]      |
| 2015 | Green tea  | Green tea leaf residue                      | HG pectin, RGII pectin, organic acids, cellulose and hemi-cellulose             | The Netherlands                        | Alkaline extraction Solvents: 0.1 M NaOH Extraction time: 2 h (protein), 5 min–24 h (carbohydrates or lignin) Temperature: 95 ºC | [119]      |
| 2015 | Papaya (Carica papaya L.) | Processing waste | Lycopene | China | Ultrasound extraction (600 W, 40 kHz) Solvents: ethanol/ethyl acetate Extraction time: 15–40 min Temperature: 20–70 ºC | [77]       |
| Year | Crop                              | Waste stream                                                                 | Target compounds          | Geographical location | Green or sustainable separation approach | References                                                                 |
|------|-----------------------------------|------------------------------------------------------------------------------|---------------------------|-----------------------|------------------------------------------|---------------------------------------------------------------------------|
| 2015 | Carrots, green beans, leeks and celeriac | Vegetable waste streams (rejected carrots, carrot steam peels, green beans cutting waste, leek cutting waste and celeriac steam peels) | Pectin                    | Belgium               | Alcohol insoluble residue Solvents: ethanol and acetone | Pectin characterization in vegetable waste streams: a starting point for waste valorization in the food industry [178] |
| 2015 | Berries of *A. melanocarpa*       | Black chokeberry wastes                                                       | Antioxidants              | France                | Extraction-adsorption process Extraction time: 2–8 h Temperature: 22 °C | Pilot scale demonstration of integrated extraction-adsorption eco-process for selective recovery of antioxidants from berries wastes [179] |
| 2015 | Cashew nuts (CNS)                 | Shells                                                                        | Anacardic acid            | Tanzania              | Review Focus on natural anacardic acids from CNS and other plants and their semi-synthetic derivatives as possible lead compounds in medicine | Potential biological applications of bio-based anacardic acids and their derivatives [180] |
| 2015 | Soy, sugarcane, tea               | Soy sauce residues, sugarcane bagasse and tea dregs                           | Hemicelluloses            | China                 | Ionic liquid Solvents: ionic liquids Extraction time: 1–5 h Temperature: 70–100 °C | Quantitative industrial analysis of lignocellulosic composition in typical agro-residues and extraction of inner hemicelluloses with ionic liquid [134] |
| 2015 | Tomatoes                          | Processing tomato                                                             | Nutritional bioactive compounds, lycopene | Italy                 | Biocompatible technology extraction | Recovery of tomato bioactive compounds through a biocompatible and eco-sustainable new technology for the production of enriched “nutraceutical tomato products” [181] |
| Year  | Crop                      | Waste stream                                                                 | Target compounds                                                                 | Geographical location | Green or sustainable separation approach                                                                 | References |
|-------|---------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------|-----------------------------------------------------------------------------------------------------------------|------------|
| 2015  | *Citrus sinensis*  (Hamlin, Valencia, Pera riu and Pera Natal) | Albedo and flavedo                                                           | Flavanone                                                                   | Brazil               | Enzymatic process tannase, pectinase and cellulase                                                                 | Simultaneous extraction and biotransformation process to obtain high bioactivity phenolic compounds from Brazilian citrus residues [110] |
| 2015  | Sunflower                 | Seeds                                                                         | Oil- (fatty acids and their antioxidant capacities) and water-soluble phase (proteins, carbohydrates and phenolics) | Slovenia              | Subcritical water extraction                                                                                   | Simultaneous extraction of oil- and water-soluble phase from sunflower seeds with subcritical water [103] |
| 2015  | Cereals, root crops, fruits, vegetables, oilseeds, meat, dairy products | Food waste                                                                   | Nutritionally interesting compounds, chemicals and biofuels                    | Brazil               | Review Sub- and supercritical technologies                                                                       | Sub- and supercritical fluid technology applied to food waste processing [89] |
| 2015  | Agricultural biomass      | By-products such as durian peel, mango peel, corn straw, rice bran, corn shell and potato peel | Bio-fuel, water soluble sugars and phenolic compounds                           | Malaysia and Nigeria | Review Sub-critical water                                                                                     | Sub-critical water as a green solvent for production of valuable materials from agricultural waste biomass: a review of recent work [182] |
| 2015  | Sugarcane                 | Sugarcane waste (rind, leaf and bagasse)                                      | Wax/long-chain aldehydes and n-policosanols (nutraceutical compounds) triterpenoids | UK and Brazil         | Supercritical CO₂ (scCO₂)                                                                                     | Sugarcane waste as a valuable source of lipophilic molecules [183] |
| 2015  | Mangoes                   | Peel                                                                          | Pectin                                                                        | Germany and Saudi Arabia | Hot-acid extraction                                                                                           | The arabinogalactan of dried mango exudate and its co-extraction during pectin recovery from mango peel [184] |
| 2015  | Coffee                    | Spent coffee grounds                                                          | Tannin compounds                                                             | Malaysia              | Alkaline extraction                                                                                                | The influence of extraction parameters on spent coffee grounds as a renewable tannin resource [185] |
| Year | Crop                        | Waste stream                                      | Target compounds                  | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|-----------------------------|---------------------------------------------------|-----------------------------------|-----------------------|----------------------------------------------------------------------------------------------------------------|------------|
| 2014 | *Eucalyptus globulus* wood  | Trimmings of *Eucalyptus globulus* wood veneers   | Phenolic compounds                | Spain                 | Aqueous two-phase extraction PEG 2000 and ammonium sulphate Extraction time: 30–390 min Temperature: 25–65 °C | [124]      |
| 2014 | Pomegranates                | By-products after winemaking of pomegranate        | (poly)phenolic compounds          | Spain, Mexico and Italy | Extraction with MeOH 70% (v/v) and sonication                                                                  | [186]      |
| 2014 | Citrus                      | Peel, pulp and seeds                               | Several value-added products, such as essential oils, pectin, enzymes, single cell protein, natural antioxidants, ethanol, organic acids, and prebiotics | Greece and Sweden     | Review                                                                                                           | [187]      |
| 2014 | Olives                      | Olive solid waste                                  | Natural dye                       | Tunisia               | Aqueous extraction in closed flasks Solvent: NaOH Extraction time: 15–120 min Temperature: 30–90 °C                | [125]      |
| 2014 | Coffee                      | Waste coffee grounds                               | Biodiesel production              | United Kingdom        | Suspended in fresh heptane room temperature                                                                    | [188]      |
| 2014 | Grapevine and hazelnut      | Grapevine waste and hazelnut skins                | Polyphenols content               | Italy and France      | UAE and MAE Solvents: ethanol, methanol, acetone, butanone, β-cyclodextrin Extraction time: 5–40 min Temperature: 20–60 °C | [58]       |
| 2014 | Bamboo                      | Raw bamboo culm                                    | Lignin                            | Malaysia              | Review Chemical and steam explosion methods                                                                     | [189]      |
| Year | Crop                          | Waste stream             | Target compounds       | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|-------------------------------|--------------------------|------------------------|-----------------------|----------------------------------------------------------------------------------------------------------|------------|
| 2014 | Spruce                        | Spruce sawdust           | Carboxylic acids       | Finland               | Alkaline extraction Solvents: Na₂CO₃ or Na₂S.9H₂O Extraction time: 30 min + 30 min; Temperature: 80 °C up to 160 °C and 210 °C | Production of carboxylic acids from alkaline pretreatment byproduct of softwood [120] |
|      | Variety of biomass sources (rapeseed, soybean, palm oil and nonedible feedstocks) | Preferably 2nd–4th generation feedstock (non-edible materials as bagasse, oil waste, microalgae, cyanobacteria and microbes) | Biodiesel             | Malaysia              | Review Supercritical fluid process and catalytic in situ or reactive extraction process                  | Integration of reactive extraction with supercritical fluids for process intensification of biodiesel production: prospects and recent advances [90] |
| 2014 | Cherries                      | Cherry seeds             | Total phenolic content | Brazil and France     | Pressurized fluid extraction (PFE) Solvent: anhydrous ethanol Extraction time: 2–10 min Temperature: 40–80 °C | Isolation by pressurized fluid extraction (PFE) and identification using CPC and HPLC/ESI/MS of phenolic compounds from Brazilian cherry seeds (Eugenia uniflora L.) [190] |
| 2014 | Corn                          | Corn stover              | Lignin                 | USA                   | Protic ionic liquid (PIL) Extraction time: 24 h Temperature: 90 °C                                       | Lignin extraction from biomass with protic ionic liquids [135] |
| 2014 | Oranges                       | Peel                     | d-limonene             | United Kingdom        | Microwave-assisted extraction 200 W, closed vessel Solvent: hexane Temperature: 70–110 °C                  | Microwave-assisted extraction as an important technology for valorising orange waste [59] |
| 2014 | Sweet Limes                   | Peel                     | Antioxidant phenolics  | Pakistan              | Enzymatic treatment Incubation time: 30–120 min Temperature: 30–75 °C pH 5 to 8                             | Optimization of enzyme-assisted revalorization of sweet lime (Citrus limetta Risso) peel into phenolic antioxidants [111] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|-------------------------------------------|------------|
| 2014 | Artichoke | Artichoke scraps | Phenolic compounds | Italy | Ultrasound-assisted extraction (UAE) Time: 60 min Solvent: water | Phenols and antioxidant activity in vitro and in vivo of aqueous extracts obtained by ultrasound-assisted extraction from artichoke by-products [79] |
| 2014 | *Cachrys pungens* Jan (Umbelliferae) | Aerial parts of *Cachrys pungens* Jan (Umbelliferae) | Bioactive compounds | Italy | Solvent extraction Solvents: methanol Extraction time: 72 h room temperature dark conditions | Phytotoxic activity of *Cachrys pungens* Jan, a Mediterranean species: separation, identification and quantification of potential allelochemicals [191] |
| 2014 | Wheat | Wheat straw | Major organic components (e.g., N-heterocycles, fatty acids, phenols and lignins) | Canada | Fast pyrolysis steel shots 475 °C | Wheat straw biomass: a resource for high-value chemicals [192] |
| 2013 | Cranberries | Cranberry juice and pomace | Polyphenolics | Canada and Mexico | Pilot scale methods Solvents: ethanol Extraction time: 24 h | Bioactivities of pilot-scale extracted cranberry juice and pomace [48] |
| 2013 | Fruits, vegetables, eggs, shrimp | Plant residues, industrial and post-harvest materials | Carotenoids | Mexico | Review Novel environmentally friendly solvents (e.g., ethyl lactate, bioethanol, vegetal oil, commercial enzymes) | Carotenoids extraction and quantification: a review [193] |
| 2013 | Tomatoes | Peels | Lycopene | Italy | Enzymatic-assisted extraction Temperature: 45 and 60 °C pH 4–5 and 9–10.5 | Environmentally friendly lycopene purification from tomato peel waste: enzymatic-assisted aqueous extraction [112] |
| 2013 | Coffee | Coffee residue left after the preparation of the brew (spent coffee grounds—SCG) | Polysaccharides | Portugal | Alkaline extraction Solvent: H₂O and 4 M NaOH Extraction time: 3 h Temperature: 20–120 °C | Extractability and structure of spent coffee ground polysaccharides by roasting pre-treatments [194] |
| Year | Crop | Waste stream       | Target compounds          | Geographical location | Green or sustainable separation approach                                                                 | References |
|------|------|--------------------|---------------------------|-----------------------|----------------------------------------------------------------------------------------------------------|------------|
| 2013 | Coffee | Spent coffee grounds | Lipids, oil               | Iran                  | Soxhlet, UAE, MAE, SFE Solvents: petroleum benzene and \(n\)-hexane Soxhlet: 6 h, boiling temperature UAE: 45 min, ambient conditions MAE: 30 s, 200 and 800 W SFE: 200–250 bar, 40–60 °C, modifier (water, ethanol, hexane) | Extraction of lipids from spent coffee grounds using organic solvents and supercritical carbon dioxide [60] |
| 2013 | Forest Industry | Forest residues, including bark | Bioactive molecules       | Canada                | Review Green alternatives for the design, formulation, and manufacture of new products with applications in various markets (cosmetics, natural health products, biocides, adhesives, coatings) | Forest extractives, the 4th pathway of the forest biorefinery concept [195] |
| 2013 | Coffee | Spent coffee grounds (SCG) | Lipid fraction            | Portugal and Brazil   | Supercritical carbon dioxide Extraction time: 1 h Temperature: 55 °C Pressure: 250 bar CO\(_2\) flow rate: 15 kg/h | From coffee industry waste materials to skin-friendly products with improved skin fat levels [91] |
| 2013 | Walnuts | Green husk         | Natural compounds with antioxidant and antimicrobial properties | Spain and Portugal   | Solvent extraction Solvents: water, methanol, ethanol Extraction time: 45 min room temperature | Influence of solvent on the antioxidant and antimicrobial properties of walnut (\textit{Juglans regia} L.) green husk extracts [49] |
| 2013 | Coffee | Spent coffee | Antioxidants              | Spain                 | Soxhlet, SPE, filter coffeemaker Solvents: water, ethanol, methanol Extraction time: 6–165 min Temperature: 80–100 °C | Influence of extraction process on antioxidant capacity of spent coffee [50] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|-----------------------|------------------------------------------|------------|
| 2013 | Tomatoes | Peel | Fatty acids | France | Depolymerization 1.5 M KOH overnight treatment at room temperature | Interfacial properties of functionalized assemblies of hydroxy-fatty acid salts isolated from fruit tomato peels [196] |
| 2013 | Coffee | Spent coffee grounds (SCG) | Polysaccharides | Portugal | Microwave superheated water extraction Extraction time: 5 min Temperature: 200 °C | Microwave superheated water extraction of polysaccharides from spent coffee grounds [61] |
| 2013 | Turkish red pine timber | Waste barks | Natural dye | Turkey | Natural dye extraction from waste barks of Turkish red pine (Pinus brutia Ten.) Timber and eco-friendly natural dyeing of various textile fibers [126] |
| 2013 | Cotton, jute, flax, hemp, ramie and natural colorants | Wastes and manufacturing by-products | Fibres, polysaccharides, dyes and pigments, polyphenols, oils and other biologically active compounds | India | Review Conventional maceration, soxhlet, MAE, SFE, ultrasonic extraction | Perspectives for natural product based agents derived from industrial plants in textile applications: a review [197] |
| 2013 | Coffee | Spent coffee grounds | Natural antioxidants | Italy | Solvent extraction Solvents: H2O, ethanol, Extraction time: 30 min Temperature: 60 °C | Recovery of natural antioxidants from spent coffee grounds [198] |
| 2013 | Feijoa fruits | Primarily skin and some flesh | Total soluble solids (TSS), pectin fibre content, total extractable PP content (TEPC) and total antioxidant activity | New Zealand | Accelerated solvent extraction Solvents: (acidified) water, ethanol Temperature: 20 or 50 °C | Utilisation potential of feijoa fruit wastes as ingredients for functional foods [127] |
| 2012 | Green tea | Green tea waste | Noncaffeine tea polyphenols | China | Water bath 20 min 90 °C | A novel way of separation and preparation non-caffeine tea polyphenols from green tea waste [199] |
Table 1 (continued)

| Year | Crop       | Waste stream                              | Target compounds                  | Geographical location | Green or sustainable separation approach                   | References                                                                 |
|------|------------|-------------------------------------------|-----------------------------------|-----------------------|-----------------------------------------------------------|---------------------------------------------------------------------------|
| 2012 | Larch      | Larch wood-derived lignocellulosic residue| Arabinogalactan, pectin, and crystalline glucose | Russia               | Water extraction                                           | An eco-friendly technology for polysaccharide production from logging and sawing waste [128] |
|      | Olives     | Olive leaves                              | Oleuropein                        | Greece                | SFE and PLE                                               | Development of a green extraction procedure with super/subcritical fluids to produce extracts enriched in oleuropein from olive leaves [92] |
|      | Wood       | Wood barks, obtained from pulp mills as industrial wastes | Natural phenolic polymers of tannins and lignin | France               | Aqueous extraction                                        | Development of green adhesives for fibreboard manufacturing, using tannins and lignin from pulp mill residues [129] |
|      | Wheat      | Wheat milling by-products                  | High quality oil and vitamin E     | Italy                 | Review                                                    | Durum wheat by-products as natural sources of valuable nutrients [200] |
|      | Tree bark  | Waste product from paper pulp industries  | Antioxidants                       | Sweden                | SFE, PFE, SLE                                             | Extraction of antioxidants from spruce (Picea abies) bark using eco-friendly solvents [93] |
|      | Timber     | Empty fruit bunches                        | Fiber                              | Malaysia              | Perspective paper                                         | Fiber resin matrix composites: nature's gift [201] |
|      | Oranges    | Peel                                      | Essential oil                      | United Kingdom        | Steam distillation and microwave irradiation              | p-cymenesulphonic acid: an organic acid synthesized from citrus waste [202] |

Extraction time: 2–3 h
Temperature: 60–80 °C

SFE: 30 MPa, 50 °C, 9.6 kg/h
PLE: 10.34 MPa, 10 min, 40–150 °C
Solvents: H₂O and EtOH

Extraction time: 1 h under reflux
Temperature: 75 °C

Extraction time: 30 min–24 h
Temperature: 70–180 °C
Solvents: scCO₂, ethanol, H₂O

Extraction time: 30 min–24 h
Temperature: 70–180 °C
Table 1 (continued)

| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2012 | Black tea | Black tea wastes | Pancreatic lipase-inhibiting polyphenols | Japan | Hot-compressed water (HCW) ion-exchange water extraction temperature: 100–200 °C | Polyphenols extracted from black tea (Camellia sinensis) residue by hot-compressed water and their inhibitory effect on pancreatic lipase in vitro [203] |
| 2012 | Green tea | Green tea waste | Polyphenols | China | Liquid-liquid extraction Solvents: H2O, glyceryl, triacetate, n-butanol, ethyl acetate Extraction time: 12 h + 2 h | Recovery of tea polyphenols from green tea waste by liquid–liquid extraction [204] |
| 2012 | Citrus | Peels | Polymethoxy flavonoids | China | Solvent extraction Solvents: methanol and ethanol Extraction time: 1–3 h Temperature: 65–85 °C | Study on the extraction technique of poly-methoxyflavonoids from citrus peels by using response surface methodology [205] |
| 2011 | Coffee | Husks | Caffeine | Spain | Supercritical CO2 Extraction time: 20 min Temperature: 323 K Pressure: 60 bar CO2 flow rate: 2–3 g/min | Extraction of caffeine from Robusta coffee (Coffea canephora var. Robusta) husks using supercritical carbon dioxide [94] |
| 2011 | Oranges | Peel | Essential oils | France and Tunisia | Microwave steam diffusion (MSDF) Extraction time: 12 min Temperature: 100 °C | Microwave steam diffusion for extraction of essential oil from orange peel: kinetic data, extract’s global yield and mechanism [62] |
| 2011 | Grape | Skins | Anthocyanins | Spain | Microwave-assisted extraction Solvents: H2O, methanol Extraction time: 5–20 min Temperature: 50–100 °C | Microwave-assisted extraction of anthocyanins from grape skins [63] |
| 2011 | Tea (green, oolong and black) | Tea residues (green, oolong and black tea residues) | Phenolic compounds | Japan | Microwave-assisted extraction water under autohydrolytic conditions Extraction time: 2 min Temperature: 110–230 °C | Microwave-assisted extraction of phenolic compounds from tea residues under autohydrolytic conditions [64] |
| Year | Crop                          | Waste stream                               | Target compounds                                                                 | Geographical location | Green or sustainable separation approach                                                                                                                                                                                                 | References                                                                 |
|------|-------------------------------|--------------------------------------------|----------------------------------------------------------------------------------|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| 2011 | Sea Buckthorn (Hippophae rhamnoides) | By-Products of juice production            | Flavonoids                                                                       | France               | Solvent-free microwave hydrodiffusion and gravity (MHG) without addition of solvent or water atmospheric pressure                                                                                                              | Solvent free microwave-assisted extraction of antioxidants from sea buckthorn (Hippophae rhamnoides) food by-products [206] |
| 2011 | Wheat                        | Wheat straw                                | Energy and CO₂ secondary metabolites including fatty acids, wax esters and fatty alcohols | England              | Supercritical CO₂ extraction Temperature: 40–100 °C, Pressure: 100–300 bar, CO₂ flow rate: 40 g/min                                                                                                                            | Use of green chemical technologies in an integrated biorefinery [95]        |
| 2011 | Olives                       | By-products generated during storage of extra virgin olive oil | Phenolic compounds, hydroxytyrosol, tyrosol, decarboxymethyl oleuropein aglycone, and luteolin | Italy and Spain       | Solid–liquid and liquid–liquid extraction Solvents: n-hexane, methanol, H₂O, Extraction time: 1 h                                                                                                                                  | Wastes generated during the storage of extra virgin olive oil as a natural source of phenolic compounds [207] |
| 2010 | Tomatoes                     | Ground tomatoes without seeds              | Lycopene                                                                         | France and Algeria   | Solvent extraction Solvent: n-limonene                                                                                                                                                                                                 | Carotenoid extraction from tomato using a green solvent resulting from orange processing waste [208] |
| 2010 | Tea plant                    | Tea stalk and fiber wastes                 | Caffeine                                                                          | Turkey               | Supercritical CO₂ ethanol as co-solvent Extraction time: 1–5 h, Temperature: 50–70 °C, Pressure: 250 bar, semi-continuous flow                                                                                                  | Effect of ethanol content on supercritical carbon dioxide extraction of caffeine from tea stalk and fiber wastes [96] |
| 2010 | Portuguese elderberry        | Pomace                                     | Anthocyanins                                                                     | Portugal             | Supercritical CO₂ extraction Solvents: CO₂, water, ethanol, Extraction time: 40 min, Temperature: 313 K                                                                                                                       | Effect of solvent (CO₂/ethanol/H₂O) on the fractionated enhanced solvent extraction of anthocyanins from elderberry pomace [97] |
| 2010 | Green tea                    | Green tea waste                            | Polyphenols, total catechins, and reducing sugars                                | South Korea and USA  | Solvents: cold water (25 °C), hot water (90 °C), sulfuric acid, hydrochloric acid and methanol, Extraction time: 20 min 250 rpm                                                                                      | Effects of cellulase from Aspergillus niger and solvent pretreatments on the extractability of organic green tea waste [130] |
| Year | Crop             | Waste stream       | Target compounds                          | Geographical location | Green or sustainable separation approach | References                                                                 |
|------|------------------|--------------------|-------------------------------------------|-----------------------|------------------------------------------|---------------------------------------------------------------------------|
| 2010 | Tea              | Tea waste          | Caffeine                                  | Iran                  | Subcritical water extraction             | Isolation of caffeine from tea waste using subcritical water extraction [104] |
|      | Citrus sudachi   | Peels              | Flavones                                  | Japan                 | Microwave-assisted extraction             | Microwave-assisted extraction and methylation of useful flavones from waste peels of *Citrus sudachi* [209] |
|      | Mate (*Ilex paraguariensis*) | Mate residue    | Compounds with antioxidant properties, such as phenolic acids and methylxanthines, such as caffeine | Brazil                | Solvent extraction                       | Phenolic acids and methylxanthines composition and antioxidant properties of mate (*Ilex paraguariensis*) residue [210] |
| 2010 | Rice             | Rice bran          | Phenolic compounds as well as other valuable materials | Japan                 | Subcritical water                        | Production of phenolic compounds from rice bran biomass under subcritical water conditions [105] |
|      | Citrus           | Peels              | Essential oil                             | France and Algeria    | Microwave hydrodiffusion gravity         | A new process for extraction of essential oil from citrus peels: microwave hydrodiffusion and gravity [65] |
| 2009 | Kiwifruit        | By-products derived from kiwifruit processing | Phenolics and pectin polysaccharides | New Zealand           | Solvent extraction                       | Evaluation of the extraction efficiency for polyphenol extracts from by-products of green kiwifruit juicing [211] |
|      | Palm             | Black liquor of oil palm waste | Lignin                                  | Malaysia              | Solvent extraction                       | Exploring the antioxidant potential of lignin isolated from black liquor of oil palm waste [212] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|----------------------|------------------------------------------|------------|
| 2009 | Turkish tea plants | Tea stalk and fiber wastes | Caffeine | Turkey | Supercritical carbon dioxide Extraction time: 1–10 h Temperature: 55–75 °C increasing pressure up to 250 bar semi-continuous flow | Extraction of caffeine from tea stalk and fiber wastes using supercritical carbon dioxide [99] |
| 2009 | Rice | Rice bran | Oil (value-added materials such as amino acids, organic acids, and water-soluble saccharides) | Japan | Subcritical water preheated oil bath: 100–180 °C Preheated salt bath: 200–360 °C Reaction time: 5 min | Sub-critical water treatment of rice bran to produce valuable materials [106] |
| 2009 | Several biomass | Residues rich in lignocellulosics | Bio-based chemicals (e.g., succinic, lactic, fumaric l-malic, l-aspartic acids) | England | Review Focus on green chemical conversion of lignin into higher value chemicals | The integration of green chemistry into future biorefineries [21] |
| 2009 | Apple | Industrially generated apple pomace | Antioxidants and polyphenols | Ireland | Pressurized liquid extraction accelerated solvent extractor static extraction of 5 min Temperature: 75–193 °C | The optimization of extraction of antioxidants from apple pomace by pressurized liquids [213] |
| 2008 | Chicory, citrus, cauliflower, endive, and sugar beet | Plant by-products (chicory roots, citrus peel, cauliflower florets and leaves, endive, and sugar beet pulps) | Pectins | France and Finland | Enzymatic extraction Extraction time: 4 h Temperature: 50 °C | Extraction of green labeled pectins and pectic oligosaccharides from plant by-products [113] |
| 2008 | Tea (green, oolong, and black) | Green, oolong, and black tea residues | Polysaccharides, polyphenols, arabinose, galactose, xylose, catechins | Japan | Microwave heating Solvent: water Temperature: 110–230 °C | Microwave heating of tea residue yields polysaccharides, polyphenols, and plant biopolyester [66] |
| 2008 | Plant lipids | Plant oils and other natural lipidic phases | Phytosterols, vitamins | Czech Republic | Review Enzymes as efficient natural catalysts | Plant products for pharmacology: application of enzymes in their transformations [114] |
| Year | Crop | Waste stream | Target compounds | Geographical location | Green or sustainable separation approach | References |
|------|------|--------------|------------------|-----------------------|------------------------------------------|------------|
| 2007 | Broccoli | Broccoli seeds | Natural sulforaphane | China and Australia | Liquid–liquid and solid-phase extraction Solvents: ethanol, hexane, ethyl acetate | Separation and purification of sulforaphane from broccoli seeds by solid phase extraction and preparative high-performance liquid chromatography [214] |
| 2006 | Tea | Tea waste | Caffeine | Turkey | Solid–liquid extraction solvents: hot water and chloroform Temperature: 370 K and 293 K | Solid–liquid extraction of caffeine from tea waste using battery type extractor: process optimization [215] |
components in these matrices, such as water or high molecular weight compounds [39].

The decision concerning the best method to separate the compounds of interest from the raw material is dependent on several aspects, such as the characteristics of the target extracts and raw material (physical–chemical properties), available technology, required purity, selectivity, stability and, more importantly here, the greenness of the whole process. As can be seen in Fig. 5, the most cited techniques in these research papers were based on solvent/maceration (25% of the total), microwave (19%), ultrasonication (14.7%) and supercritical fluid processing (13%), followed by methods using ionic liquids (7%), enzymatic and subcritical fluid treatment (6%), as well as the association of two or more techniques.

According to the literature, the most widespread approaches for separating natural products from a number of matrices are based on liquid–liquid or solid–liquid extraction (LLE and SLE). Several greener alternatives have been proposed by replacing toxic or non-renewable organic solvents, as well as the extraction times. In some cases, solid-phase extractions (SPE) were also carried out and decreased both the amount of solvent and the number of extraction cycles, offering high enrichment factors [39, 40]. Actually, the mass transfer enhancement for SLE has been largely studied and applied, contributing to technology innovation, process intensification and integration, and energy saving, especially important for microwave, ultrasound, and high-pressure processing, for instance [41]. An overview of these techniques and related examples will be discussed in this section.

Fig. 5 Main green and sustainable techniques used to separate natural products from waste described in research papers (ISIS Web of Knowledge, January 2006 to December 2017)
3.1 From Conventional Solvent Separation to Enhancement Processing Approaches Over the Last 10 Years

Solvent processing is one of the most traditional methods to remove natural products from bio-derived materials. In this extraction approach, the raw material in adequate size is exposed to different solvents, mostly organic, which remove soluble components of interest. The samples are then usually centrifuged and filtered to separate the solid residue, and the extract is used in this way (as a food supplement or for preparing functional foods, for example) or treated after this step. Solvent extraction is attractive compared to other methods due to low cost and simplicity. However, this method does not always use benign solvents; it frequently requires an evaporation/concentration step for recovery, it usually demands large amounts of solvent and needs a long time to be carried out. Additionally, the possibility of thermal degradation of natural bioactive components is also possible due to the high temperatures used during the extraction process [42]. Despite this, it is largely used in industries, where solvent reuse is of great economic importance. In general, the raw material (in its liquid or solid form) is mixed with a solvent, and the separation kinetic of the target compounds is influenced by parameters such as the solvent ratio, pH, and temperature and, for SLE, the particle size. The solvent should be atoxic, non-flammable and stable at working conditions, ideally renewable and cheap, with low viscosity and an adequate boiling point, allowing for easier solvent removal from the extract/fraction [43]. Recently, several models have been proposed to predict the best solvents to be used in a specific case, which do not only take into account physical descriptors, such as enthalpy of vaporization, dielectric constant, refractive index, boiling point, etc., but also empirical descriptors to evaluate, for instance, intermolecular forces (specific and non-specific solute–solvent interactions, e.g., hydrogen bond donor and/or hydrogen bond acceptor, Van der Waals and ion/dipole forces). Purely theoretical descriptors have been also introduced, offering the most important advantage of not requiring any experiments, as is the case of the model known as quantitative structure property relationship (QSPR), able to predict 127 polarity scales for more than 700 solvents [44].

The solvent selection also depends on the physical–chemical proprieties of the compounds of interest, considering principally the selectivity and greenness degree of the process, aiming at obtaining high recoveries and the integrity of the target compounds. In general, the raw material stays in contact with the solvent for a certain period (from minutes to days), when the soluble compounds are transferred from the matrix to the extractor phase, usually by shaking the system. For SLE, the dispersion of the particles in the solvent is facilitated agitating them, optimizing their contact and accelerating the separation process. Traditionally, solvent treatment is performed at room temperature, although heating can promote higher recoveries to these compounds that are not thermosensitive. In some cases, LLE and SLE can be time-consuming, demanding further purification and concentration steps, which are their main drawbacks [41, 45].

Maceration using green and non-toxic solvents for the separation of natural products from plant-derived waste has been described over the last years (e.g., to remove dyes from quince leaves or catechins, theaflavins, gallic acid, and antioxidants in
general from walnut green husk, cranberry pomace, black tea and banana processing waste). According to these studies, using water, methanol, ethanol or a mixture of them at 70–100 °C can be a low-cost, benign alternative for the recovery of high added-value compounds derived from residual biomass [46–49]. Scaling-up was also studied, whose results showed to be useful in determining industrial process feasibility and the economic value of polyphenols for commercial use, increasing the overall profitability of the cranberry industry [48].

Whenever possible, higher temperatures allow for higher mass transfer in a shorter time with lower energy consumption in general, resulting in better recovery efficiency than conventional systems [50]. As observed in Fig. 5, the second most cited green and sustainable separation process is based on microwave heating and can be considered a non-conventional technique nowadays. Heating is based on non-ionizing electromagnetic waves. Those between 0.915 and 2.45 GHz are used for industrial, scientific and medical applications. The overall principle of heating is rooted in its direct impact with polar materials/solvents and is dependent on ionic conduction and dipole rotation, occurring simultaneously in most cases. The increased temperature can overcome the natural product-matrix interaction caused by Van der Waals forces, dipole attraction, hydrogen bonding of the compounds of interest and active sites in the matrix. Therefore, thermal energy can disrupt both solute–solute and solute–matrix interactions, providing the activation energy required for the desorption process. The mass transfer of the compounds from the raw material to the solvent is also accomplished by convection and diffusion mechanisms, causing the explosion of plant cells and releasing their content into the liquid phase [51].

The eco-friendly removal of essential oils, pectin and polyphenols from a number of plant raw materials mediated by microwave irradiation has been described over the last years, paying special attention to citrus waste [52–66]. In fact, the orange juice processing industry can be considered more than a good case study. This sector is highly wasteful, generating 50% of waste from the total fruit/starting material (e.g., peel, bagasse, seeds and yellow water). Around 20 million tonnes of orange peel per year are produced worldwide, which consist of water (80%) and sugars, cellulose, hemicellulose, pectin and $\Delta$-limonene (20%). Recently, it was shown using a mathematical model that $\Delta$-limonene extraction consisted of a two stage diffusion process for a microwave (MW) heating approach: initial extraction from the exterior of cells followed by trans-membrane diffusion. Compared to other conventional extraction methods, it was found that the microwave treatment was more efficient, resulting in a higher overall yield due to the access to a higher amount of $\Delta$-limonene [59].

The successful microwave-assisted solvent-free modification of pectin derived from citrus waste has also been reported [53]. These approaches not only allow for the separation of the major components of citrus peel, but they also add further value through the production of other high value-added products, such as pectin, $\Delta$-limonene and a rare form of mesoporous cellulose which are produced in a single step, without added acid [67]. Along these lines, the concept of dry-biorefinery is gaining momentum, since valuable products can be recovered from plant by-products without adding solvents or water, using green processes such as MW [56].
Innovation relies on the separation of the target compounds from raw materials, which are rich in water, achieved without adding solvents or water, illustrating a circular systemic process; i.e., all materials and resources could be reintegrated into the integrated and zero-waste biorefinery [19]. Although very attractive, as expected, the design and use of real MW industrial scale equipment requires additional studies related to safety, corrosion and maintenance intervals [68].

The combination of two or more extraction/concentration methods is quite common in the literature (Table 1). As described by Boukroufa et al. [56], the removal of essential oil, polyphenols and pectin from orange waste was conducted using microwave and ultrasound technology, without adding any solvents. Essential oil separation was performed by Microwave Hydrodiffusion and Gravity (MHG), and thereafter the remaining water of this process was used as a solvent for the subsequent extraction of flavonoids and pectin. For polyphenol separation, ultrasound-assisted extraction (UAE) was used, and response surface methodology (RSM) using the central composite design (CCD) approach was used to investigate the influence of some variables. The CCD revealed that the optimized conditions of ultrasound power and temperature were 0.956 W/cm² and 59.83 °C giving a polyphenol yield of 50.02 mg GA/100 g dm, which, compared to conventional extraction, promoted an increase of 30% in the yield. Pectin was extracted by microwave-assisted extraction, resulting in a maximal yield of 24.2% for microwave power of 500 W (3 min), whereas traditional extraction provides 18.32% (120 min). As can be seen, the combination of microwave, ultrasound and recycled water resulted in higher recoveries of the compounds of interest in a shorter time, so that a systemic loop/cycle could be closed using only the resources generated in the plant. This makes the whole process optimized in terms of time, energy savings, cleanliness and reduced amount of waste.

As can be noted, ultrasound has been widely utilized for helping to extract target components from waste plant-derived sources, reducing separation time, solvents, energy consumption and improving the product quality. The effectiveness of ultrasound is attributed to the cavitation phenomenon, assisting the solubilization of the compounds of interest into the solvent, enhancing their removal from the bulk raw material [69]. According to Chemat [70], the ultrasound waves (from 20 kHz to 10 MHz) pass through an elastic medium, inducing a longitudinal displacement of particles resulting in a succession of compression and rarefaction phases in this medium. Every medium has a critical molecular distance and, below this critical point, the liquid remains intact. However, above this distance, the liquid would break down, creating voids (cavitation bubbles) in the liquid. When the size of these bubbles reaches a critical point they collapse, releasing a large amount of energy. The estimated temperature and pressure at this time are estimated at 5000 and 2000 K atmospheres. This creates hotspots that accelerate the chemical reactivity into the medium, generating microjets directed towards the solid surface, also responsible for the general higher effectiveness of this technique, as the high pressure and temperature involved in the process destroy the cell walls of the plant matrices and their content can be released into the medium more easily.

Some new process aiming at agro-industrial waste application in food industries based on ultrasound-assisted extraction of natural products have been reported
[71–79], as is the case of carotenoid separation from pomegranate peels using different vegetable oils as solvents [72]. Sunflower and soybean oils were used as solvents and parameters such as time, temperature, solid/oil ratio used were analyzed considering the yield. It was found that the optimum mild operating conditions were: extraction temperature, 51.5 °C; peel/solvent ratio, 0.10; amplitude level, 58.8%; solvent, sunflower oil. Additionally, a subsequent separation of oil and carotenoids was not necessary, since the pigmented oil can be used as a carotenoid source in different commercial products in this format.

The green recovery of cellulose from oil palm bunches by autoclave-based and ultrasonication pre-treatments were successfully developed to replace the non-green chlorite method [73]. An ultrasonic process with hydrogen peroxide yielded 49% cellulose with 9.13% alpha-cellulose content and 68.7% crystallinity, as compared to 64% cellulose with an autoclave treatment. The cellulose/polypropylene composites generated with high tensile strength, high thermal stability, and low water and diesel sorption showed great potentials for conversion into eco-composite products such as polymeric material insulated cables for high voltage engineering, automotive parts, sports tools and other household or office items.

Another highly cited green and sustainable technique to isolate organic compounds from bio-based waste is based on supercritical fluid processing (Fig. 5). It is widely known that substances at temperatures and pressures near or above their critical points have exceptional solvent characteristics for analytical purposes. These supercritical fluids possess liquid-like solvating and gas-like diffusivity power, and other tuneable properties that can be adjusted varying temperature, pressure and the addition of other components acting as a modifier. Due to its gas-like low viscosity and high diffusivity, the supercritical fluid can easily penetrate into plant materials with a fast mass transfer rate. Possibly, the most important property of supercritical fluids for separation processes is diffusion, obtaining solubility and diffusion good enough to provide quantitative extraction yield [80, 81]. Carbon dioxide (scCO₂) is the fluid most widely used for extractions, with critical parameters of 31.1 °C and 73 atm (7.39 MPa), at relatively low operating conditions. It behaves as a nonpolar or polarizable solvent and low molar mass alcohols (co-solvents) are often added in small quantities to modify the solvent polarity. Because carbon dioxide can be depressurized to the gaseous state, the solvent is easily removed and supercritical fluid-based separation methods are easily coupled with subsequent analysis. Therefore, scCO₂ provides miscibility to the majority of natural products, availability and low cost, reliably high purity, negligible toxicity, facility for removal and reuse, resulting in many advantages for downstream processing in terms of product purification and/or catalyst recycling [80].

The approach using scCO₂ has been widely used for isolation and purification of chlorophylls, carotenoids, lipids, alkaloids, antioxidants from matrices such as filter tea, spruce bark, tomato and elderberry pomace, grape, passiflora, coffee and cupuassu seed waste [82–99]. In addition to the optimization of the separation process, some studies also aim to evaluate the techno-economic viability of large-scale commercial production, for example, to obtain cupuassu butter from cold-pressed seed residues, also evaluating the influence of thermodynamic and kinetic variables of yield, chemical composition and production costs of the extracts [86].
conditions related to extraction kinetics, chemical composition and production costs were 30–35 MPa and 50 °C. It was shown that the phenolic content (0.47–2.82 mg/g) was lower than those commonly found using other methods (20–23 mg/g). The high contents of tocopherols, as well as the unsaturated fatty acids (48%) compared to the saturated fatty acids (52%) present in the butter obtained by scCO2 demonstrated its great potential as an ingredient in food, pharmaceutical and cosmetic industries. In addition, process intensification for biodiesel production involving supercritical fluids has been reported [84, 90]. Such approaches can allow biodiesel production without any addition of catalyst, or via catalytic in situ or reactive extraction process, combining the extraction and reaction phase together in a single operation unit. These studies also discuss both processes towards the future bio-refinery setup and more efficient use of all waste produced.

The use of fluids different to CO2 has been described in the literature, but as they are usually organic solvents, they do not show any distinct advantages and often have high critical temperatures. Despite having a very high critical temperature, water shows unique properties in the subcritical region (200–300 °C), as a reduction in dielectric constant (20–30) and density (0.7–0.8 g/cm³) compared to water at room temperature, improving its ability to dissolve nonpolar organic and inorganic compounds. Under these conditions, the water dissociation constant into hydroxide and hydrogen ions are more than three orders of magnitude higher, so that near-critical water acts as a self-neutralizing acid or base catalyst, avoiding salt waste generation. Moreover, using subcritical and supercritical water conditions greatly simplifies the product purification step in some cases, since nonpolar products are insoluble in water in lower temperatures [80, 100–106].

Other potential scalable approaches have been described, such as enzymatic [107–114], alkaline [115–120] and based on different types of aqueous media (e.g., cyclodextrins, montmorillonite K-10/LiOH, green liquor) [121–130]; ionic liquids [131–135], deep eutectic solvents [136–138], constituting alternative methods for the recovery of high added-value compounds from agro-industrial waste aiming at obtaining the best analytical, economical and socio-environmental compromise [139–142].

Based on the investigated literature [143], Table 2 summarizes the advantages and disadvantages of the four most cited green and sustainable techniques.

4 Conclusions

The establishment of vanguard biorefineries for bioeconomy and circular economy urgently demands innovation in green and sustainable separation for the recovery of natural products from agro-industrial by-products all over the world. Sustainable separation includes the idea of integrated valorization not only in an economic sense, but also strengthens other social and environmental dimensions, from small to large producing scales. According to the literature over the last decade, the number of studies in this field has grown significantly in recent years. New approaches incorporating holistic extraction and/or purification techniques, also integrating systemic chemical transformation through the design and use of renewable materials.
### Table 2  Advantages and disadvantages of different technologies that were most cited as green and sustainable techniques over the last 10 years

| Technology              | Advantages                                                                                   | Disadvantages                                                                 |
|-------------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Solvent processing      | Inexpensive and simplicity; allows for solvent reuse                                        | Does not always use benign solvents; frequently requires an evaporation/concentration step for recovery; usually demands large amounts of solvent and long extraction time; possibility of thermal degradation |
| Microwave processing    | Reduced extraction time; reduced solvent usage; improved extraction yield; simple and inexpensive | Not good when either target compounds or solvents are non-polar or volatiles |
| Ultrasonication         | Inexpensive, simple and efficient; can reduce the operating temperature (good for thermolabile compounds); can be used with any solvent | Its efficiency may be linked to the nature of plant matrix; the active part of ultrasound inside the extractor is restricted to a zone located in the vicinity of the ultrasonic emitter |
| Supercritical fluid     | Moderate extraction temperature (good for thermolabile compounds); rapid mass transfer (larger extraction rate); solubility of a chemical in a supercritical fluid can be manipulated; can eliminate concentration process; the solutes can be separated from supercritical fluids without losing volatiles due to its extreme volatility; additional filtration or centrifugation to remove solid residue is not necessary | Onerous operating conditions |

and optimized processes should combine the best green analytical figures of merit with online evaluation of the whole production chain. These approaches should generate healthier and more efficient products, methods and processes at an affordable and fair cost.

Overall, solvent processing and its modification towards the enhancement of mass transfer to remove the compounds of interest from selected waste have been widely used (25%), also on industrial scales. Alternative extraction or purification methods have shown increasingly more applications, such as for microwave, ultrasonication and supercritical fluid processing. It was shown that a wide range of natural products and their derivatives are used mainly in food (as dyes, aromas, flavors) in medicines or green formulations in agriculture. According to the data available, one paradigmatic case largely studied is the valorization of citrus waste, representing more than 10% of all residues considered in the research papers.

Moreover, an emergent challenging topic is to evaluate biorefinery processing alternatives, i.e., sustainability assessment tools, for example LCA, which include parameters such as feedstock supply (to verify the suitability and adequacy of a potential biomass feedstock for the separation or transformation treatment), process performance (to assess the input–output balance of material and energy flows) and bio-based chemical production [144]. Therefore, the decision about the best separation approach takes into account various fundamental aspects and is based on green and sustainable assessment tools, considering the type of agro-industrial waste (e.g., quantity, periodicity, chemical variability, water amount, distance to the processing unit), the natural target products (chemical quality, purity, humidity, costs etc.) and available technologies.

Using sustainability indicators and tools will be increasingly demanded in this field, contributing to the greenness or sustainability of the whole processing system. The development of a sustainable separation method which provides better recovery efficiency will not only add value to the agro-industrial waste, reducing the overall manufacturing costs and the use of synthetic chemicals, but will also aggregate value to the whole production chain, including its final products. The emergence of bio-based industries is changing the current status of the producing systems, contributing to the current biomass residual losses. Based on the literature, the scenario for future research and innovation in green and sustainable separation for the recovery of agro-industrial waste is truly beginning, bringing together various areas and sectors towards more efficient and circular systems.

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