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Green Solvents for the Extraction of High Added-Value Compounds from Agri-food Waste

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Abstract

Large amounts of agri-food by-products, non-edible food, and waste are produced throughout the supply chain from the initial production to the final consumption stages. The valorization of this biomass to obtain high value-added compounds has been the focus of extensive research in the last decade. For this purpose, the use of green techniques is essential to reduce the negative impact on the health and the environment. In this review, we discuss the use of green solvents for the valorization of agri-food waste and by-products, and we consider their potential to replace conventional organic solvents in order to provide more environmentally friendly and sustainable processes. The use of supercritical fluids, neoteric (ionic liquids and deep eutectic solvents), bio-based, and supramolecular solvents is critically dicussed. Parameters affecting extraction efficiency are detailed for each type of solvent along with advantages and limitations for application at the industrial scale.

Keywords Agri-food waste · Green solvents · Valorization · Bio-based solvents · Ionic liquids · Deep eutectic solvents

Introduction

Agri-food waste is estimated at 5 billion tons of biomass residues per year globally [90]. Only in EU, the total annual biowaste is estimated at 76.5–102 million tonnes [61]. Nowadays, the final disposal of agri-food waste has become a major challenge for food processing industries due its potential negative impact on the environment [45]. Thus, agri-food by-products account for 3.3 billion tonnes of carbon dioxide emissions each year, globally.

The Food and Agricultural Organization (FAO) estimates that one-third of the edible food is annually wasted [49]. The valorization of non-edible crop residues is also relevant (peels, seed, leaves, pits, pulp, press cakes). Over the last years, the evaluation of these by-products as sources of biologically active compounds has attracted great interest [22] both to decrease the volume of residues and to obtain high added-value compounds [126]. Natural bioactive compounds from agri-food waste constitute a wide variety of molecules with different structures and functionalities for the production of nutraceuticals, functional foods, and cosmetics, such as polyphenols, lycopene, anthocyanins, lipids, sugars, alkaloids, proteins, dietary fibers, and flavors ([70]; see Table 1). Articles reviewing the valorization of certain industrial food waste, such as tomato [126], wine [62, 129], fruit juice [62], and olive oil [8, 111], have been reported in the last years. Other valorization activities include the production of animal feed, compost, fuel, wood-based panels, bio-fertilizers, and biofibers.

Many efforts have been devoted to find simple and inexpensive strategies for the exploitation of agri-food by-products. A variety of solvents and extraction methods, such as high pressure and temperature extraction, supercritical fluids, ultrasound-, and microwave-assisted extractions, and enzymatic treatment have been proposed in an attempt to enhance process efficiency for recovery of high added-value compounds. Organic solvents, such as diethyl ether, *N,N*-dimethylformamide, ethanol, hexane, toluene, and their aqueous solutions have been the main extractant phases [17]. However, many of the solvent-based extraction processes are nowadays considered inefficient because of the extended times needed to extract/purify the target compounds, the requirement of large solvent volumes per sample so that a high amount of toxic waste is generated. This waste possesses a negative impact on health, safety, and the environment [134] and consequently, the search for solvent reduction consumption and greener solvents has been strongly fostered [35, 102, 130].

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Table 1 High added-value compounds in agri-food waste (examples)

By-product	Compounds	Use and/or benefitial effects
Yellow pitahaya	Vitamin C, polyphenols	Vitamin C: dietary supplement (essential nutrient for repair of tissues, enzymatic production of certain neurotransmitters, immune system functions), antioxidant; Polyphenols: antioxidants
Mangostino peel	Anthocyanins	Food coloring, antioxidants
Orange peel	Flavonoids, phenolics compounds	Antioxidants
Avocado peel and avocado seed	Essential oils, fat acids	Fragances and flavorings, food additives and preservatives
Grape seed	Resveratrol, polyphenols, anthocyanins	Antioxidants (resveratrol is used as dietary supplement too)
Passion fruit	Polyphenols	Antioxidants
Pineaple peel	Enzymes	
Soursop peel	Flavonoids	Antioxidants
Guava peel	Vitamin C	Dietary supplement, essential nutrient, immune system functions, antioxidant
Papaya peel	Phenolic compounds	Antioxidants
Pupunha peel	Polyphenols	Antioxidants
Cocoa peel	Polyphenols	Antioxidants
Tamarind peel	Aromatic compounds	Fragances
Coffee peel and spent coffee grounds	Polyphenols	Antioxidants
Tomato peel and seed	Lycopene	Food coloring, antioxidant
Corncob	Lignin, glucose and xylose	Paper industry, textiles and fibers, food and pharmaceuticals additive, building materials, biofuel
Coconut husk	Celullose, lignin	Paper industry, textiles and fibers, food and pharmaceuticals additive, building materials, biofuel

Green Solvents: Potential and Limitations in the Extraction and Valorization of Agri-food Waste

Green solvents are non-toxic, non-volatile, recyclable, biodegradable, and may not involve a high energy cost of synthesis [38]. A number of alternative solvents that fulfill, to a greater or lesser extent, this definition are included in Fig. 1. They are grouped in four categories, namely, supercritical fluids, neoteric, bio-based, and supramolecular solvents. Replacement of a harmful solvent by a greener alternative in a separation process is not trivial and, in some cases, novel challenges and limitations can arise due to the different physicochemical properties of the solvents considered. In this review, we discuss briefly the extraction potential and limitations of green solvents for the valorization of agri-food waste.

Supercritical Fluids

Supercritical fluids (SCFs) are substances for which both pressure and temperature are above their critical values [19, 67]. The SCFs are characterized by gas-liquid properties, i.e., gas-

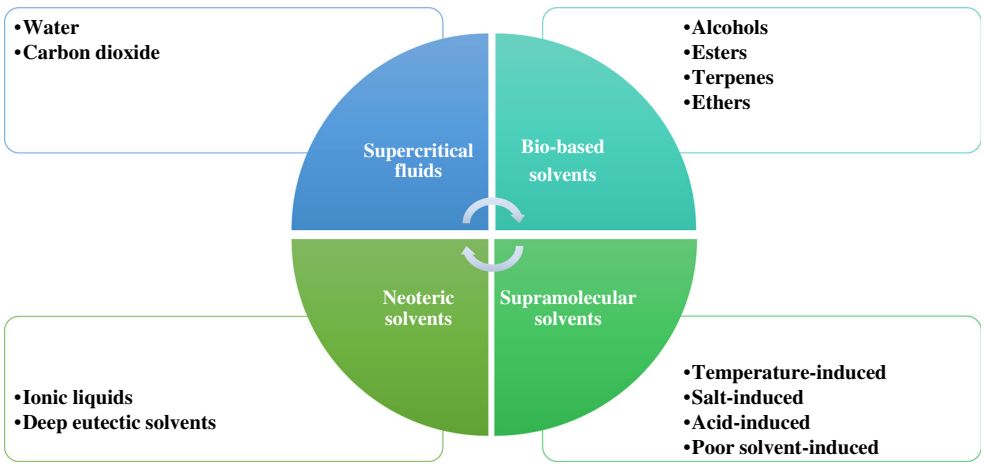

Fig. 1 Green solvents covered in this review

like viscosity and diffusivity and liquid-like density and solvating properties. This makes them excellent solvents for extraction processes in the so-called supercritical fluid extraction, SFC [67, 105]. Thus, the fluid diffuses easily through solids and provides faster extraction yields [36]. Additionally, the SCF density can be modified by changing its pressure and/or temperature and since density is related to solubility, the solvent strength of the fluid can be modified [53]. Furthermore, the fluid solubility strength can be tuned by the addition of modifiers. This versatility makes SFCs very interesting for different applications [146].

SCFs have been extensively used in the industry and scientific literature for fractionation of products, dyeing of fibers, treatment of contaminated soils, production of powders in micro/nanometer sizes and novel chemical reactions to replace organic solvents (e.g., catalytic hydrogenation reactions typical for petrochemical industry), energy industry applications, and biofuel production [67]. The most used SCFs are water, carbon dioxide, helium, refrigerants, and hydrocarbon fuels, but health and safety benefits are especially evident in the use of supercritical CO_2 and supercritical water.

Water

Water is considered as the cleanest solvent. Supercritical water exists at temperatures above 374 °C and pressures above 22.1 MPa. Supercritical water behaves as a nonpolar solvent because hydrogen bonding is lost under these extreme conditions [40]. Its use has increased during the last two decades and industrial applications have been developed looking for environment-friendly and energy-saving technologies [46, 142]. However, despite extensive research efforts, corrosion problems have not been satisfactorily solved for application at industrial scale up to now [106]. An alternative is the use of pressurized hot water extraction (PHWE) or subcritical water extraction that uses water at temperatures above its boiling point (100 °C) but below the critical point of water (374 °C, 22.1 MPa) [96, 97, 106]. A variety of applications to the extraction of bioactives have been made, such as flavonoids from onion waste [89], pectin from jackfruit peel waste [76], phenolic compounds from grape skin [63], or reducing sugars from wheat straw [1]. However, the risk of hydrolysis and other degradation reactions during extraction are major drawbacks of this technique [106].

Carbon Dioxide

Supercritical fluid (SCF) extraction with carbon dioxide has widely contributed to the development of green extraction processes for bioactive compounds [36]. CO_2 is the most used because of its moderate critical temperature (31.3 °C) and pressure (7.38 MPa). CO_2 is non-carcinogenic, non-toxic, non-mutagenic, non-flammable, and thermodynamically stable [67] and generally recognized as safe [53].

The applicability of SFE to high added-value compounds from vegetable matrices (agri-waste, algae, etc.) has been reviewed by several authors [19, 36, 42, 67, 94, 121]. The bioactive compounds extracted by SFE include a wide variety, such as phenolic compounds from passion fruit seeds [95], grape seeds [103], and papaya seeds [24], phytochemical compounds from soy bean expeller [6], essential oil from orange peel [141], phenols from olive oil mill waste [72], phytosterol from roselle seeds [93], limonoid glucosides from grapefruit molasses [147], solanesol from tobacco waste [138], and saponins from Agave salmiana bagasse [117] (see Table 2). Most of these studies investigate the influence of pressure and temperature in the extraction yield. Extractions are usually carried out at temperatures and pressures in the ranges 35–80 °C and 10–70 MPa, respectively. The flux ranges from 1.5 to 5000 mL CO_2/min and the extraction times from 25 to 150 min. The use of experimental design is common for understanding linear and complex interactions among variables. However, as [121] pointed out, the successful application of an experimental design in SFE relies on the in-depth understanding of both SFE and experimental design techniques [121].

When compared with other extraction techniques, CO_2-SFE was superior to ultrasound-assisted extraction for isolation of essential oils from orange peel extracts [141], while for more polar compounds, such as phenolics from olive oil mill waste, CO_2-SFE was acceptable but less efficient than extraction with polar solvents (e.g., ethanol). In this sense, many authors propose the use of co-solvents, such as ethanol, for improving recoveries of polar and medium polar compounds [16, 21, 141]. Since CO_2 is a gas with low polarity, the addition of a polar solvent (4.7–10%) improves its solubility for compounds with polar functional groups (such as vitamin E, γ-oryzanols, and xanthophylls). Another advantage of SFE processes is the fact that this technology can be easily transferred at industrial scale to extract large quantities of matrix and obtaining great amount of extract in a single step [21].

However, despite the excellent extraction properties and great versatility, the high processing costs and the complex industrial equipment are limiting factors. For example, the economical assessment of SFE into a sugarcane-microalgae biorefinery by Albarelli et al. [3] led to the conclusion that the process was not economically attractive, as it increased the total investment by 71% (respect to traditional biorefinery) and presented a very high energy demand that would lead to high operational costs [3].

Neoteric Solvents

Neoteric solvents is a term that refers to solvents structurally novel or unconventional and usually characterized by physical

Table 2 Extraction of bioactive compounds from agroindustrial by-products using SCFs and subcritical water

Agri-food waste	SCFs	Sample size	Extraction rate/time	Bioactive compound	Extraction efficiency/performance	Reference
Soy bean expeller	CO_2 at 35 °C and 40 MPa, 3% w/w ethanol	50 g	0.5 kg/h	Phytochemical compounds	Up to 16.0 mg GAE/ 100 g and up to 65 mg QE/ 100 g	[6]
Grape seeds	CO_2 at 40 °C and 30 MPa	6 g	1.5 mL/min	Phenolic compounds	25 mg GAE/g	[103]
Maritime pine bark	CO_2 at 30 °C and 25 MPa, 10% v/v ethanol	-	95–167 g/min, 90 min.	Catechin+epicatechin	0.35 mg/g	[16]
Onion skin	CO_2 at 40 °C and 10 MPa, 4.7% v/v ethanol	1 g	10.5 mL/min, 120 min	Phenolic compounds	3.7 mg/g quercetin 1.4 mg/g protocathechiuc acid (among others)	[21]
Orange peel	CO_2 at 50 °C and 40 MPa	0.5 g	1.6 mL/min, 15 min	Limonene, β-myrcene, decanal, α-pinene, linalool, valencene	~ 0.25% limonene; ~ 0.004–0.005% linalool, β-myrcene and decanal; ~ 0.003–0.004 % α-pinene, linalool, valencene	[141]
Rice bran	CO_2 at 43 °C and 34.5 MPa, 10% ethanol	4 g	60 min	Rice brain essences (with vitamin E, total γ-oryzanols and total xanthophylls)	0.68–16.65, 1410–2480, and non deected-0.1 μg/g of vitamin E, γ-oryzanols and xanthophylls	[124]
Brazilian cherry seeds	CO_2 at 45 °C, 17 MPa, 10% ethanol	72 g	2 g CO_2/min, 22 h	Sesquiterpenes (Germacrone and γ-Elemene)	380 mg/g germacrone and 460 mg/g γ-elemene	[116]
Kalahari melon and Roselle seeds	CO_2 at 60 °C and 30 MPa (melon) and at 80, °C and 20 MPa (roselle seeds)	1 g	20 mL/min, 3 h	Tocopherol	266.87 and 94.88 mg/100 g from Kalahari melon and roselle seed	[92]
Citrus junos seed	CO_2 at 70 °C and 50 MPa	5 g	3 mL/min, 120 min	N-methylanthranyl acid methyl, β-sitosterol, squalene	1.1, 1.85 and 0.11 x 10^4 mg/g of N-methylanthranyl acid methyl, β-sitosterol and squalene, respectively	[132]
Olive oil mill waste	CO_2 at 25 °C and 35 MPa	2 g	2 g/min, 60 min	Phenolic compounds	0.76% (w/w)	[72]
Roselle seeds	CO_2 at 40, °C, and 40 MPa, 10% v/v ethanol	-	20 mL/min	Oil with phytosterol	108.7 % recovery of oil containing 7263 mg/Kg of phytosterol	[93]
Grapefruit molasses	CO_2 at 50 °C and 48.3 MPa, 10% v/v ethanol	60 g	5 L/min, 40 min	Limonoid glucosides	0.61 mg/g molasses	[147]
Industrial tobacco waste	CO_2 at 40 °C and 30 MPa	7 g	1 L/min, 120 min, pretreatment with organic solvent extraction	Solanesol	0.9 % (with pretreatment), 0.1 % (without pretreatment)	[138]
Agave salmiana bagasse	CO_2 at 60 °C and 30 MPa, 10% v/v ethanol	10 g	1.7 g/min, 60 min	Antioxidants	17.6 μmol Trolox equivalents/g	[117]
Apple by-products	Water, 125 °C (flavonoids) and 175 °C (polyphenols) and 10.3 MPa	5 g (11 mL cells were filled with water)	3 min	Phenolic compounds	1.8 μmol GAE/g 1.3 μmol QE/g	[107]
Onion waste (skin)	Water, 230 °C (flavonoids) and 175 °C (polyphenols) and 3 MPa	0.6 L water suspension of onion peel (2% wt solids)	30 min	Phenolic compounds	63-75 mg GAE/g 23-26 QE/g	[89]
Potato peel	Water, 90 °C and 4 MPa	0.5 g	3 mL/min, 9 min	Carbohydrates and phenolic compounds	610 mg glucose equivalent/g 20 mg GAE/g	[5]

and chemical properties that can be finely tuned for a range of applications by varying the chemical constituents [50]. Among neoteric solvents, fluorous solvents, ionic liquids, and eutectic solvents have received the highest attention.

Fluorous solvents are made from highly fluorinated compounds, such as perfluorooctane, perfluorohexane, perfluoro (methyl cyclohexane), perfluorodecaline, perfluorotributylamnine, and perfluoropolyether [84]. They are so-called the "third liquid phase," because of their immiscibility with both water and organic phases, which make their reuse and application easier in separation processes. Furthermore, perfluorocarbons have advantages as solvents because they are chemically unreactive, and non-flammable and have low toxicity [64]. Main drawbacks are their high cost, limited applicability to very non-polar solutes, and the concern about their sustainability due to their high environmental persistence and global warming potential (greenhouse gases) [29]. Fluorous solvents have been employed for extraction of metals and organic compounds. However, to the best of our knowledge, their applicability to the extraction of bioactive compounds for agri-waste has not been explored yet. So, in this review, we focus our discussion on ionic liquids and eutectic solvents.

Ionic Liquids

Ionic liquids (ILs) have been widely applied to the extraction of bioactive compounds [101, 133]. They are a class of salts composed of discrete cations and anions with melting points below 100 °C [52], unique physicochemical properties and pre-organized and tunable solvent structures [127]. Some of their special properties are negligible vapor pressure, excellent thermal and chemical stability, wide electrochemical potential window, and outstanding solubility for organic, inorganic, and organometallic substances. These properties, along with the extraordinary degree of tunability for both cations and anions, make ionic liquids interesting materials for extraction processes [52].

Although the use of ILs in food processes is not regulated by the Federal Drug Administration (FDA) [82], the extraction of alkaloids, terpenoids, flavonoids, phenolic compounds, saponins, etc. from natural sources (mainly plants) has been widely investigated [133]. However, their applicability to agri-food waste is somehow more limited (see Table 3). Among ILs, 1-alkyl-3-methylimidazolium-based ILs are by far the most studied and are usually combined with $[BF_4]$, Cl^-, and Br^- counterions. The application of greener ILs, e.g., ammonium-based cations, such as cholinium, is still scarce [133].

Regarding agri-food waste, ILs have been applied to the extraction of reducing sugars from corn stalk [74] and soybean hulls [56], levulinic acid from rice husk [65], lactic acid from deoiled cottonseed cake, wheat straw and sugarcane bagasse [47], oleanolic acid from olive tree leaves [30], cellulose from coconut husk [148], tyrosol from olive mill wastewater [73], and lignin from sugarcane bagasse [113]. The use of high temperature for extraction is usual (up to 140 °C) as well as long extraction times (2 h); additionally, ultrasonic extraction has been frequently reported. The viscosity of ILs is high and can be lowered by temperature, which is an important factor in the mass tranfer process and fluid flow [65]. Additionally, the high temperature promotes the biomass dissolution [54] and ILs are mostly thermally stable above 200 °C [65]. IL concentration and composition are the other most investigated parameters for extraction processes based on these solvents.

A special advantage of ILs for the extraction of bioactives is their ability to permeate and modify biomass cell walls and tissues and facilitate the release of compounds. Protic ILs may facilitate the hydrolysis of polysaccharides and other components for cell lysis via strong hydrogen bonding. This has been exploited for the extraction of asthaxanthin for algae and levulinic acid from lignocellulosic biomass [65, 120]. The extraction of levunilic acid also involved a catalytic process favored by acidic ILs [65]. Acidic ionic liquids have been proposed for further favoring the hydrolysis of lignocellulosic materials [74].

The versatility of ILs and the wide range of experimental conditions for its use make them very attractive for extraction processes. However, their further practical use has been limited so far, mainly due to their inherent high costs and potential toxicity. The development of more environmentally benign ILs for extraction purposes is still in its infancy [43, 101]. To reduce costs, the utilization of co-solvents, such as methanol, and solvent reuse based on the different solubility of ILs and bioactives in organic solvents and water, are available options [31]. Thus, Khan et al. [65] proposed the recycling of the IL by re-extraction of levulinic acid with ethyl acetate (in which the IL was not soluble) and solubilization of the IL in water (in which levunilic acid was not soluble). The IL was then recovered by evaporation using vacuum rotary and could be reused four times with reasonable yield. The yield of levulinic acid was between 47 and 48%. Saha et al. [113] proposed to recycle the IL and to recover lignin from soybean hulls by adding a mixture of acetone: water (1:1 v/v) to the bagasse:ionic liquid solution 10:1 (v/v). This caused the precipitation of the cellulosic material and left a filtrate solution containing lignin and the IL. Ligning was recovered after evaporation of acetone and the IL was obtained after the further evaporation of water under vacuum. The yield of lignin for the whole process was 90.1% and the efficient recovery of the IL was proved by thermogravimetric analysis.

Deep Eutectic Solvents

Deep eutectic solvents (DESs) were developed to overcome the environmental issues of ILs [43]. They have physical and chemical properties comparable with ionic liquids, but they are easier to synthesize and more stable and cost-competitive and, typically, most of them are environmentally friendly

Table 3 Extraction of bioactive compounds from agroindustrial by-products using ILs

Agri-food waste	Type of ILs	Ratio sample size (g):ILs volume (mL)[a]	Extraction conditions	Bioactive compound	Extraction efficiency/ performance	Reference
Corn stalk	C_4mimBr, C_4mimCl, C_4mimHSO_4, C_6mimCl, 1-Allyl-3-methylimidazolium chloride, **C_4mimCl**	0.2:4	100 °C , 60 min, HCl/sample ratio 7%	Total reducing sugars	71%	[74]
Rice husk	[C4(Mim)2][(2HSO4)(H2SO4)0], **[C4(Mim)2][(2HSO4)(H2SO4)2]** C4(Mim)2][(2HSO4)(H2SO4)4]	0.025:0.75	110 °C , 60 min IL:water 10:1	Levulinic acid	47.52%	[65]
Olive tree leaves	[C6mim]Cl, [C8mim]Cl, [C10mim]Cl, **[C12mim]Cl**, [C12mim]Br, [C12mim]I, **[C14mim]Cl**, [C16mim]Cl and [C18mim]Cl	1:10	80 °C for 2 h or microwave-assisted extraction for 30 min; IL in water (500 mM)	Oleanolic acid	2.5 % (wt%)	[30]
Coconut husk	[N2220][HSO4]	9:100 w/w IL:water 80:20 v/v	120 °C, 2 h	Cellulose, lignin	56.5% (cellulose) 12.8% (lignin)	[148]
Olive mill wastewater	**[P4441][Tf2N]**, [N4441][Tf2N], and [N8881][Tf2N]	1:5	30 °C, 2 h	Tyrosol	78%	[73]
Sugarcane bagasse	C_3mim acetate	1:20 w/w	140 °C, 120 min	Lignin	90.1%	[113]
Soybean hulls	[C4(Mim)2] hydrogen sulfate + pretreatment with 1-allyl-3-imidazolium chloride [AMIM]Cl	1:4.8 w/w	95 °C, 1 h; ultrasonic-assisted extraction; water/sample 20:1	Reducing sugars	275.4 mg/g	[56]

[a] Or per gram when indicated (% w/w); optimal ILs shown in bold; $C_n$mim: 1-alkyl-3-methylimidazolium cation; [Tf2N]: bis(trifuoromethylsulfonyl)imide anion; [N2220]: Triethylammonium catión; [N4441]: tributyl(methyl)phosphonium catión; [N8881]: tricaprylmethylammonium; [P441]: tributylmethylphosphonium cation

[119, 150]. DESs have shown a great potential in emerging green extraction technologies and they are expected to be widely transferred to industry in coming years [4].

DESs are eutectic mixtures of Lewis or Brønsted acids and bases which can contain a variety of anionic and/or cationic species [123]. They are usually produced by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor. The charge delocalization trough the hydrogen bonding results in a decrease of the melting point of the mixture. This is due to the fact that DESs consist of large, non-symmetric ions with low lattice energy and hence, low melting points [123].

DESs are prepared by simply mixing the components and are classified depending on the nature of the complexing agent into four categories (see Fig. 2). They can be composed of a quaternary ammonium salt and a metal chloride (type I), a metal chloride hydrate (type II) or a hydrogen bond donor (type III) and of a hydrogen bond donor and a metal chloride (type IV). A range of hydrogen bond donors have been studied such as amides, carboxylic acids, and alcohols [123].

One of the attractive features of DES is their tunability. Thus, a huge number of eutectic mixtures with varying viscosity, density, miscibility, and polarity can be obtained by simply changing one or both components in the mixture. In this way, DESs can be easily tailored for specific applications including extraction processes [33, 59, 130].

Regarding the applicability of DESs in the valorization of agri-waste, type III DESs have been the most studied and have the greater potential in biomass processing due to their quick and easy preparation, non-reactivity with water, biodegradable nature, and cost effectiveness [80, 123]. The most used DES has been made up of choline chloride (ChCl) mixed with different chemical functional groups such as amine, alcohol, acid, and sugar, which act as hydrogen bond donors. Choline is non-toxic, have low cost, and is classified as a provitamin in Europe [123].

DESs have been reported for the extraction of tocols from crude palm oil [51], anthocyanins from wine [15, 109], genistin, genistein and apigenin from Pigeon pea roots [32], and lignin from rice straw [55, 69] and anthocyanins from grape pomace [100]. Polyphenols have been extracted from lemon peels, olive leaves, onion solid wastes, red grape pomace and wheat bran [87, 98], grape skins [109], Cajanus cajan leaves [140], Morus alba L. leaves [152], olive pomace [26], and spent coffee grounds [145]. The extraction time and yield for the bioactives varied according to the type of DES, the structure of the bio-compound, the extraction temperature applied and the use of auxiliary energy (such as microwave or

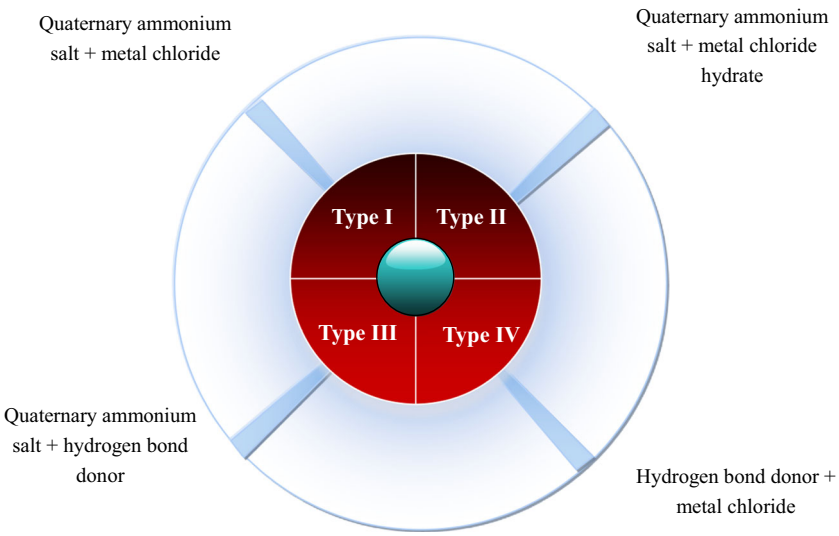

Fig. 2 DES clasification. Adapted from Smith et al. [123]

ultrasound). Extraction times varied from 11 min to 24 h with temperatures in the range 40–90 °C and frequent dilution with water (5–30 % w/w). Table 4 lists valorization processes of agri-waste with DESs.

The physicochemical properties of DESs greatly influence extraction rates [149]. Polarity and viscosity are two very influencial factors when optimizing the extraction of bioactive compounds with DESs. The high viscosity of DES is a major disadvantage since it reduces the mass transfer of bioactive compounds. Viscosity can be lowered by increasing the temperature at which extraction occurs and by mixing DES with water. For instance, in the case of DESs made up of ChCl:glycerol (1:1), the viscosity decreased by 1/5 at 5% of water and to 1/80 at 20% of water [149]. Additionally, the polarity of DES increased along with the water content [57]. Different hydrogen bond donors (i.e., sugars, polyhydric alcohols, and organic acids) were tested by Cui et al. [32] to lower viscosity and increase polarity of choline-based DESs in the extraction of genistin, genistein, and apigenin from pigeon pea root [32]. The viscosity of DESs with sugars was the greatest while the polarity was higher for sugars and polyhydric alcohols compared with organic acids. Finally, DESs made up of 30% water in 1,6-hexanediol/ChCl (7:1, mol/mol) were selected as optimal. Microwave-assisted extraction and 80 °C were applied to enhance the extraction yield.

Procedures for the recovery of DES and bioactives with solvent back-extraction, such as a washing step with water:ethanol for ChCl:glycerol enriched with glucose and xylose and further drying at 38 °C, have been proposed [108]. In this way, the yield of glucose and xylose were in the ranges 91.5–92.3% and 59.5–95.5 %, respectively. Hadi et al. [51] investigated the reuse of other chloine-based DES after extraction of tocols from crude palm oil. A mixture of water–hexane (4:1 v/v) was employed for liquid-liquid separation. The hexane layer contained the tocols that were later recovered by evaporation at 60 °C. The DES-rich layer, which contained a mixture of methanol, water, and traces of hexane, was dried to remove methanol and water (15 h). The yield of the recycled DES decreased from 18,525 ± 882 to 11,741 ± 566 mg/kg (total tocols concentration). Other procedures have been described for the recovery of DES after extraction. Ruesgas-Ramón et al. [112] reviewed the use of DES for the extraction of phenolic compounds from plants. Authors reported that the use of solid-phase extraction was also a common strategy for the recovery of DES by using different types of resins (e.g., ME-2 polystyrene matrix, XAD-16 styrene–divinylbenzene). Once the extract was loaded, DES was recovered with water while a second elution step with ethanol or methanol was employed to recover the phenolic compounds. Finally, the addition of an anti-solvent for the bioactive compounds, usually water, was used to strongly dilute the DES and break the supramolecular interactions between components (losing of DES' solvation properties) which led to the precipitation of the extracted compounds.

Bio-based Solvents

Bio-based solvents are defined as solvents produced from renewable biomass sources such as energy crops, forest products, aquatic biomass, and waste materials [90]. They are produced in a biorefinery [137] which aims for the maximum recovery and production of high added-value products [23]. Some bio-based solvents are alcohols (ethanol), esters (ethyl lactate), glycerols, terpenes, furfurals (furfural, furfural alcohol, levulinic acid), and furan [75]. Viscosities are low, which make them easy to handle in extraction processes. Despite their great potential, the scale of biorefineries is still mainly limited to lab-scale or pilot plants [137]. However, some of them are already commercially available.

Table 4 Extraction of bioactive compounds from agroindustrial by-products using DES

Agri-food waste	Type of DES	Ratio sample size (g):DES volume (mL)[a]	Extraction conditions	Bioactive compound	Extraction rate efficiency/ performance	Reference
Crude palm oil	choline chloride (ChCl):acetic acid, **ChCl: malonic acid**, ChCl: citric acid	1:3 w/w	3 h IL diluted in methanol, sample diluted in hexane	Tocols	14,689-18,525 mg/kg	[51]
Wine lees (*Merlot grapes*)	ChCl:citric acid, **ChCl: malic acid,** ChCl: oxalic acid, ChCl: glucose, ChCl: fructose, ChCl: xylose, ChCl: glycerol	1:60	30 min and ultrasound-assisted extraction water in NADES 35.4 w/w	Anthocyanins and related compounds	5.2-6.5 mg/g (total anthocyanins)	[15]
Pigeon pea roots	ChCl:sucrose ChCl:1,2-propanediol, ChCl: glucose, ChCl: sorbitol, ChCl: glycol, ChCl: glycerol, ChCl:1,3-Butanediol, ChCl: 1,4-Butanediol, **ChCl: 1,6-Hexanediol**, glucose: L-proline, glucose: lactid acid	2.5:100	11 min, 80 °C, microwave-assisted extraction	Genistin, genistein apigenin	0.449 mg genistin /g, 0.617 mg genistein/g and 0.221 mg apigenin/g	[32]
Rice straw	Lactic acid: betaine; **lactic acid: ChCl**	0.5-10, 1:10 w/w	12 h ,60 °C DES with 5% water v/v	Lignin	68 mg/g	[69]
Lemon peels, olive leaves, onion solid wastes, red grape pomace, spent filter coffee and wheat bran	**Glycerol: choline chloride**/sodium acetate, glycerol: sodium–potassium, tartrate:water	0.1:10	90 min, 80 °C, –ultrasound-assisted extraction DES and 10 % water	Phenolic compounds	88.03 mg GAE/g in onion solid wastes (with glycerol: sodium–potassium, tartrate:water), 53.76 mg GAE/g in lemon waste peels, 36.75 mg GAE/g in olive leaves, 53.63 mg GAE/g in red grape pomace, 22.59 mg GAE/g in spent coffee grounds and 17.78 mg GAE/g in wheat bran	[87]
Corncob	**ChCl: glycerol**, **ChCl: imidazole**, ChCl: urea	1:16	15 h, 80 °C (ChCl: imidazole) 15 h, 180 °C (ChCl: glicerol) Washing and evaporation to remove DES + enzymatic treatment	Fermentable sugar	Glucose 91.5-92.3% Xylose 59.5-95.5 %	[108]
Grape skins	ChCl: glucose, ChCl: fructose, ChCl: xylose, ChCl: glycerol, **ChCl: malic acid**	1:10	50 min, 65 °C, ultrasound-assisted extraction	Phenolic compounds, anthocyanins	91 mg/g polyphenols and 24 mg /g anthocyanins	[109]
Cajanus cajan leaves	ChCl: glycerol, ChCl: 1,4-butanediol, ChCl: ethylene glycol, ChCl: glucose ChCl: sucrose, **ChCl: maltose**, ChCl: sorbitol, ChCl: citric acid, ChCl: malic acid, ChCl: lactic acid, citric acid: glucose, citric acid: sucrose,	1:30	12 min , 60 °C, microwave-assisted extraction DES and 20% water	Phenolic compounds (n = 14)	Stilbenes cajaninstilbene acid 6.9 mg/g; longistyline C 4.4 mg/g	[140]

Table 4 (continued)

Agri-food waste	Type of DES	Ratio sample size (g):DES volume (mL)[a]	Extraction conditions	Bioactive compound	Extraction rate efficiency/ performance	Reference
	lactic acid: glucose, lactic acid: sucrose					
Corncob	ChCl: lactic acid, ChCl: glycolic acid, ChCl: levulinic acid, ChCl: malonic acid, ChCl: glutaric acid, ChCl: oxalic acid, ChCl: malic acid, ChCl: ethylene glycol, **ChCl: glycerol**	1:20 w/w	24 h, 90 °C enzymatic treatment	Lignin removal and glucose yield	71.3 % (lignin); 96.4% (glucose)	[151]
Grape skins	ChCl: glycerol ChCl: oxalic acid ChCl: malic acid ChCl: sorbose **ChCl: proline: malic acid**	1:10	50 min, 65 °C, ultrasound-assisted extraction DES and 25% water	Flavonoids	~ 25 mg/g (sum of anthocyanins and cynidine-3-O-glucosides)	[34]
Morus alba L. leaves	ChCl: Urea, ChCl: Ethylene glycol, ChCl: Glycerol, **ChCl: Citric acid**, ChCl: malic acid, Betaine: levulinic acid, betaine: lactic acid, betaine: glycerol, proline: malic acid, proline: Glycerol, L-proline: levulinic acid, L-proline: lactic acid	1:20	30 min, 40 °C, ultrasonic-assisted extraction DES:water 3:1 v/v	Phenolic compounds	22.66 mg/g	[152]
Olive pomace	**ChCl: citric acid**, ChCl: lactic acid, ChCl: maltose, ChCl: glycerol	1:12.5	30 min, 60 ° , homogenate-assisted extraction 20% v/v water	Phenolic compounds	35 mg GAE/g and homogenization	[26]
Spent coffee grounds	ChCl: urea, ChCl: acetamide, ChCl: glycerol, ChCl: sorbitol, ChCl: ethylene glycol, ChCl: 1,4-Butanediol, **ChCl: 1,6-hexanediol**, ChCl: malonic acid, ChCl: citric acid, ChCl: fructose, ChCl: xylose, ChCl: sucrose, ChCl: glucose	1:17	45 min, ultrasonic-assisted extraction DES and 30% water	Phenolic compounds	15 mg GAE/g	[145]

[a] or per gram when indicated (% w/w); optimal DES shown in bold; GAE: gallic acid equivalents

Alcohols

The first generation of bio-based ethanol was derived from sources like starch, sugar, animal fats, and vegetable oil. The main problem was the food-versus-fuel debate [99]. The second generation was produced from a non-food biomass, such as lignocellulosic materials. The third generation was derived from microalgae [99]. Methanol can also be produced from biomass, but it has toxicity issues [137]. Other bio-alcohols with low toxicity are bio-butanol, bio-2-octanol, bio-1,3-propanediol, and bio-1,3-butanediol [20]. On the other hand, glycerol has been widely obtained as by-product in biodiesel production [137].

Esters

Ethyl acetate is an industrially relevant ester, non-toxic, and fully biodegradable [25]. This bio-solvent is mainly produced by esterification of acetic acid and ethanol in liquid or vapor phase, acetylation of ethylene, and ethanol dehydrogenation [114]. Yeasts, such as *Saccharomyces cerevisiae*, *Wickerhamomyces anomalus*, and *Kluyveromyces marxianus* can also convert sugar into ethyl acetate [68]. Ethyl lactate is widely used as a green solvent to replace chlorinated hydrocarbons [104]. It is very suitable and environmental benign for food applications. It is also allowed as pharmaceutical and food additive by the FDA [14].

Terpenes

α-Pinene is a bicyclic monoterpene hydrocarbon and is one of the most abundant components in the essential oils of various plant species [66]. It has potential for the pharmaceutical, bioenergy, fine chemistry, and flavor industries [91]. D-Limonene is a colorless liquid cyclic terpene extracted from orange peels in orange juice industry. It is widely accepted for cosmetics and food [28]. Finally, p-cymene is another bio-based molecule. It is used for the synthesis of p-cresol and fine chemicals for perfumes, fungicides, and pesticides and as a solvent of dyes and varnishes [81]. It can be obtained for conversion of limonene into p-cymene, also is present in pine trees [143].

Extraction of Compounds from Agroindustrial By-products Using Bio-based Solvents

The extraction of bioactive compounds from agri-food waste with bio-based solvents have been applied in a lesser extent than with SCFs. Studies are mainly focused on extraction from algae or natural resources (not residues) [13, 14, 39, 135]. Table 5 shows research studies concerning the use bio-based solvents to extract bioactive compounds from agri-waste.

Bio-based solvents have been used to extract rosmarinic and caffeic acids from basil wastewater [96, 97], carotenoids and phenols from tomato waste [44, 122, 125, 127], polyphenols, flavonoids, anthocyanins and ellagic acid from pomegranate peel [83], phenolic compounds, flavonoids and sinapine from seeds of rapeseed, mustard crambe and sunflower [85], phenolic compounds from lotus by-products [58], oil from rice bran [77], and volatile compounds from Cooperage woods in winemaking [2]. Ethyl lactate and ethyl acetate, sometimes in mixtures with water, have been by far the most used bio-based solvents. It is usual to employ high temperatures (usually 30–80 °C) and repetitive extractions to reach adequate recovery of bioactives, which is highly dependent on extraction time and the presence (or not) of auxiliary energy such as microwave or ultrasound.

Bio-based solvents have been reported to extract bioactive compounds as efficiently (or with higher efficiency) than conventional organic solvents. In the extraction of rice bran oil, the use of D-limonene showed superior extraction yield (24.6%) than hexane (18.6%). Similarly, in olive oil extraction, the use of D-limonene increase the lipid yield in 8.3% more than hexane [136]. Yara-Varón et al. also reported that cis-pinane and d-limonene extracted more carotenoids from carrot than n-hexane (95.4, 94.8 and 78.1% respectively) [144]. Commonly, energy-assisted extraction techniques are used for enhancing recoveries. Thus, ultrasound extraction increased in 9.4% the lycopene yield in tomato pomace with ethyl lactate–ethyl acetate mixtures [122]. Also, pressurized liquid extraction was suitable for the extraction of phenolic compounds from basil waste using mixtures of water (75% v/v) and ethanol or ethyl lactate at 150 °C, with extraction rates up to 93.9 an 99.2% respectively [96, 97].

Supramolecular Solvents

Supramolecular solvents (SUPRASs) are nanostructured liquids produced in colloidal suspensions of amphiphiles by spontaneous, sequential phenomena of self-assembly, and coacervation [18]. Coacervation is defined as “the separation into two liquid phases in colloidal systems. The phase more concentrated in colloid component is the coacervate, and the other phase is the equilibrium solution” [60].

These nanostructured liquids have been used for extraction since Watanabe and Tanaka in 1978 developed a method to extract zinc using “a micellar solution of a non-ionic surfactant that separates in two phases” also known as the cloud point technique [139]. The name SUPRAS was introduced later, to highlight the differences between these liquid phases and molecular and ionic solvents, to underline the nanostructures formed by non-covalent interactions and to emphasize the synthesis process, which is based on amphiphile self-assembly [12].

Table 5 Extraction of bioactive compounds from agroindustrial by-products using bio-based solvents

Agri-food waste	Solvent	Relationship Sample(g):solvent (mL)	Extraction conditions	Bioactive compound	Extraction rate or extraction efficiency	References
Distillation wastewater of basil	Ethyl lactate: water 25:75 % v/v	0.250 g:-not specified	Pressurized liquid extraction, 50 °C, 10 MPa, static mode, 20 min	Rosmarinic acid (RA), caffeic acid (CA)	104.1 and 94.2% for rosmarinic acid and caffeic acid, respectively	[96, 97]
Tomato waste (skin and seeds)	Ethyl lactate and ethyl acetate	1:10	30 min, 70 °C	Carotenoids	243 mg/kg (ethyl lactate) and 46.21 mg/kg (ethyl acetate)	[125]
Tomato waste (skin + seeds)	Ethyl lactate	1:10	40 min at 20 °C and 40 min at 60 °C with ultrasound-assisted extraction	Phenolic compounds, flavonoids and lycopene	1.4 mg GAE/g (20 °C), 0.5 mg catechin/g (20 ° C) and 0.05 mg lycopene/g (60 °C)	[44]
Pomegranate peel	Ethyl acetate	1:4	Soxhlet extraction, 6 h	Phenolic compounds, flavonoids, anthocyanins, punicalagings, ellagic acid	2.4-3.2 mmol GAE/g; 0.7 mmol rutin/g;0.05-0.4 μmol cyaniding-3-O-glucoside/g; punicalagings 6.8-7.3 mg/g; ellagic acid 37.7-63.6 mg/g	[83]
Seeds of rapeseed, mustard, crambe and sunflower	Ethyl acetate/water (70:30)	1:5	Overnight with shaking+45 min with ultrasound-assisted extraction; pretreatment for defafting with petroleum benzene	Phenolic compounds, flavonoids and sinapine	2.6–9.2 mg TPC/g, 2.1–59.8 mg flavonoids/g and 0–60.9 mg sinapine/g	[85]
Olive leaves	Glycerol (60% in water) + 7% w/v 2-hydroxypropyl-β-cyclodextrin	1:50	180 min at 60 °C	Phenolic compounds	54.3 mg GAE/g	[88]
Apple pomace	Ethyl acetate	1:20	3 times extraction for 3 s each and microwave-assisted extraction	Phenolic compounds, flavonoids	~ 200 mg GAE/L and ~ 150 mg rutin/L	[48]
Potato peel	Ethyl acetate	1:10	30 °C (several extraction steps)	Phenolic compounds	44-83 mg GAE/g	[9]
Olive leaves	Aqueous glicerol (9.3 w/v)	1:60	80 °C, 165 min	Phenolic compounds	51.9 mg GAE/g	[7]
Tomato pomace	Ethyl lactate + 35% v/v ethyl acetate	1:100	20 min at 63.4 °C, ultrasound-assisted extraction	Lycopene	1.3 mg/g	[122]
Cooperage woods in winemaking	Ethyl lactate	1:3	10 min 80 °C in 2-extraction cycles and pressurized liquid extraction	Phenolic compounds, volatile compounds (natural flavoring)	15 mg GAE/g ~ 30 μg/g (volatile compunds as sum of total furanic compounds, β-methyl-γ-octalactones and terpenes and norisoprenoids)	[2]
Tomeate peel and seeds	Ethyl lactate	1:10	30 min at 70 °C	Lycopene, carotene, lutein	166.4 mg lycopene/kg, 26.4 mg carotene/kg and 10.8 mg lutein/kg	[127]

The SUPRAS synthesis is made in two steps. First, "an aqueous or organic colloidal suspension of the amphiphile is prepared above its critical aggregation concentration." This suspension contains supramolecular aggregates, typically aqueous or reverse micelles or vesicles [12]. The formation of these architectures primarily depends on the packing parameter, which in turn depends of the volume and the length of the hydrophobic segment and the cross-sectional area of the head group [79].

In the second step, the generated nanostructures self-assembly in larger aggregates by the action of an external stimulus (coacervating agent) that diminishes the repulsion among the aggregates [118] and separate from the bulk solution as an immiscible liquid via coacervation ([11], p.; [110]). The most used stimulus for the coacervation are pH, temperature, inorganic, and organic salts and poor solvents for the amphiphile [12] (see Fig. 3).

Supramolecular solvents have a unique array of physicochemical properties that render them very attractive to replace conventional organic solvents in extractions [11]. Thus, SUPRAS offer mixed-mechanisms for solute solubilization and produce high extractions rates for solutes covering a wide polarity range. Multiple binding interactions are available which depends on the nature of the amphiphile [11], and due to its internal structure, different polarity regions are generated [12]. Another important characteristic is that they can be tailored to offer programmed characteristics such as molecular-restricted access behavior [10].

SUPRASs have proved high efficiency for the separation, preconcentration, or purification of organic compounds such as such as polycyclic aromatic hydrocarbons, pesticides, surfactants, bioactive compounds and dyes [12, 18]. In terms of green chemistry, they are good alternatives to the conventional extraction systems because of their high performance, low toxicity, and low cost [12, 18, 78, 115]. Furthermore, they are non-volatile and non-flammable and many amphiphiles are bio-compatible and renewable, such as carboxylic acids and rhamnolipids. In summary, sustainable and economical SUPRAS-based extraction processes can be implemented taking into account that the synthesis can be developed with green natural amphiphiles at low cost and thought energyless processes [12].

Despite their great potential, only a few studies have been related to the extraction of bioactives from agroindustrial by-products (Table 6). These studies have focused on the extraction of polyphenols from wine sludge [27], betaine from beet molasses [86], saponins from sisal (*Agave sisalana)* waste [41], and anthraquinones from aloe peel [128].

The most used amphiphiles were non-ionic surfactants from the Triton X series and the most employed coacervating agent was the temperature. High recoveries have been reported with these solvents. Good recoveries have been also obtained with other non-ionic surfactants, such as those reported by Chatzilazarou et al. [27] [27]. Thus, recoveries found for phenol from wine sludge were 98.5% using PEG 8000 as amphiphile (at pH 2.5, 55 °C) in a fast process that took 30 min. On the other hand, Ribeiro et al. [41] found that SUPRASs were superior for extraction of saponins from sisal waste (98.4%) compared with an ethanolic solution 30% v/v (38.6%) under the same conditions of time (4 h), temperature (50 °C) and sample mass/volume ratio (0.17 g/mL) [41].

Recently, SUPRAS made up of inverse aggregates of 1-hexanol in mixtures ethanol:water have been proposed for the recovery of alkaloids and polyphenols from spent coffee grounds [131]. In this case, the coacervating agent was water (poor solvent for the amphiphile) and the extraction was rapid (1 min) and made at room temperature. SUPRAS components (1-hexanol, ethanol, and water) are authorized for food processing or as food additives so that further industrial implementation is facilitated. Furthermore, extracts showed good antioxidant and antimicrobial properties.

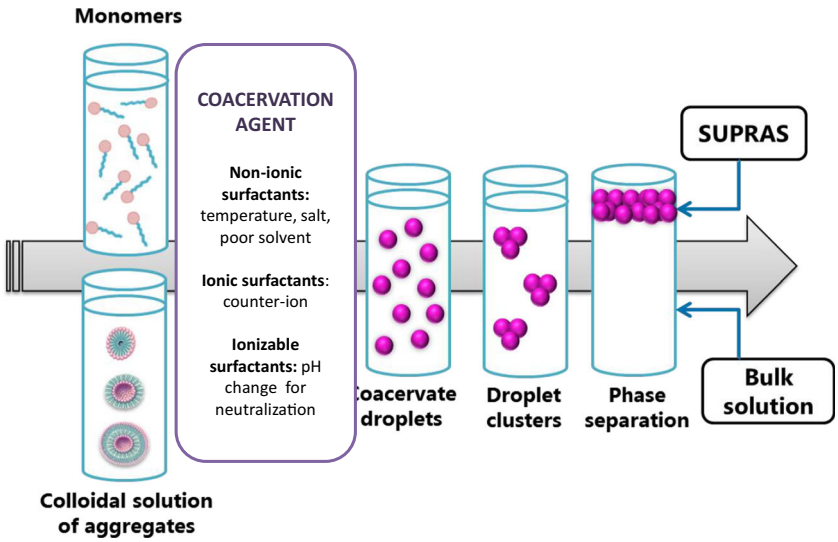

Fig. 3 SUPRAS sequential formation process by self-assembly and coacervation

Table 6 Extraction of bioactive compounds from agroindustrial by-products, using supramolecular solvents

Raw material	Amphiphile	External stimulus for phase separation and extraction conditions	Bioactive compound	Extraction rate or extraction efficiency	References
Wine sludge	Genapol X-080, **PEG 8000**	Stimulus: temperature conditions: 10 mL sample, NaCl 5%, 10% v/v of PEG 8000 (pH 3.5, 55 °C, 30 min)	Phenolic compounds	98.5%	[27]
Beet molasses	**Triton X-114,** Triton X-100, Sodium dodecyl sulfate, Cetyltrimethyl ammonium bromide	Stimulus: temperature conditions:surfactant concentration 0.5% (w/v), molasses concentration 27.5% (w/v), incubation time 20 min, pH 6.1, extraction time 30 min	Betaine	80%	[86]
Sisal waste	Triton X-100	Stimulus: temperature and salts conditions: ratio sisal/solvent 0.17 g/mL, surfactant concentration 7.5% (v/v), sodium carbonate 20% (m/v), 50 °C, extraction time 4 h	Saponins	89.1%	[41]
Aloe peel	Triton X-114	Stimulus: temperature, acids, salts conditions: surfactant concentration 10% (w/v), NaCl 2.0% (w/v) l, 40 °C, pH 3.0, extraction time 20 min	Anthraquinones	96.9%	[128]
Spent coffe grounds	**1-Hexanol**, decanoic acid	Sitimulus: water (poor solvent for the amphiphile) conditions: 24% v/v 1--hexanol, 30% v/v ethanol and 46% v/v water, extraction time 1 min	Caffeine, 5-CGA, and total phenolic compounds	3.32 mg caffeine g^{-1}; 4.3 mg 5-CGA g^{-1}; 60.1 mg 5-CGAE g^{-1} (TPC)	[131]

The recovery of bioactives from the surfactant-rich phase has been investigated by some authors. Thus, Mohammadzadeh et al. [86] proposed the back-extraction of betaine (nearly 100%) from beet molasses from the surfactant-rich phase with an aqueous phase at pH 2.5. The recovery of bioactives from the surfactant-rich phase by a change of pH in aqueous solution was also proposed by Tan et al. [128] for the recovery of anthraquinones from aloe peel with an efficiency of 70%.

Future Perspectives

This review aimed to provide an overview of the application of green solvents for the extraction of different classes of bioactive compounds from agri-food waste, mainly small organic extractable compounds (phenolic compounds, carotenoids, tocols, among others) and other high added-value compounds (fermentable sugars, lignin, oils, etc.). Research in this area is increasing in the last years and constitutes an urgent demand since disposal of agri-waste represents both cost and potential negative impact on the environment. In general, it can be concluded that if properly selected, green solvents are able to afford high extraction yields in different agri-food wastes. The sustainable character and costs associated with the extraction depend on the selected solvent, the source of bioactive compound, the temperature and processing time and the presence—or not—of assisted extraction modes, such as the use of microwave, ultrasound, or the use of re-flux.

Despite the efforts made by different authors to develop alternative green solvents and to evaluate different extraction approaches and conditions, many studies are still based on ionic liquids and SFCs. However, the use of SCFs is too expensive and the toxicity of ILs is controversial. Bio-based solvents, natural deep eutectic solvents (NADES) and supramolecular solvents appear to be a more promising and greener option due to their bio-compatibility and low toxicity. The term NADES refers to deep eutectic solvents synthetized from natural compounds, i.e., choline chloride, mixed with natural acids, amines, and alcohols [37]. For these non-volatile (or hardly volatile) green solvents, strategies for the recovery or back-extraction and concentration of bioactives are key for their implementation at industrial scale. However, only few studies investigate possible procedures. Kumar et al. [71] evaluated a biorefinery process for ethanol production from cellulose coming from rice straw. NADES was used as a pretreatment step for delignification, recovery of high purity lignin and xylan, enzymatic hydrolysis, and production of cellulosic ethanol. The study concluded that the proposed biorefinery was effective and economically viable mainly based on the possibility of solvent recovery and reuse, the cheap and energyless synthesis of NADES (lactic acid + choline chloride + water) and the coextraction of value-added products.

The evaluation of the economic viability and implementation at industrial scale are necessary to broaden the applicability for green solvents. Furthermore, studies covering the comparison of different types of green solvents for the same application or of a green solvent with conventional ones would be desirable to further understand the advantages and disadvantages of the different strategies. The development of cost-

effective and more sustainable extraction and separation processes is the critical step toward the recovery and commercialization of new and low-cost bioactive products for the nutraceutical, cosmetic, and pharmaceutical sectors. Research in extraction processes with green solvents needs to take into account in the near future: (i) the life cycle analysis of their processes and products, (ii) processes able to be scaled-up, and (iii) economic analyses of the extraction process, solvent, and material costs.

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GAE, gallic acid equivalents (total polyphenolic content); *QE*, quercetin equivalent (total flavonoids contents)

GAE, gallic acid equivalents

Optimal amphiphile in bold; *5-CGA*, 5-chlorogenic acid; *5-CGAE*, 5-chlorogenic acid equivalents; *TPC*, total phenolic compounds

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