

Applications of Nonconventional Green Extraction Technologies in Process Industries: Challenges, Limitations and Perspectives

Gertrude Fomo *, Tafirenyika Nyamayaro Madzimbamuto and Tunde Victor Ojumu

Department of Chemical Engineering, Faculty of Engineering & the Built Environment,
Cape Peninsula University of Technology, Bellville Campus, Bellville 7553, South Africa;
MadzimbamutoT@cput.ac.za (T.N.M.); OjumuT@cput.ac.za (T.V.O.)

* Correspondence: FomoG@cput.ac.za or fomogertrude@gmail.com; Tel.: +27-83-758-6805

Received: 2 April 2020; Accepted: 13 May 2020; Published: 28 June 2020

Abstract: This study reviewed five different nonconventional technologies which are aligned with green concepts of product recovery from raw materials on industrial scale, with minimal energy consumption and chemical use. Namely, this study reviewed supercritical fluid extraction (SCFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), ultrasound extraction (UAE) and pulsed electric fields extraction (PEFE). This paper provides an overview of relevant innovative work done in process industries on different plant matrices for functional value-added compounds and byproduct production. A comparison of the five extraction methods showed the supercritical CO₂ (SC-CO₂) process to be more reliable despite some limitations and challenges in terms of extraction yield and solubility of some bioactive compounds when applied in processing industries. However, these challenges can be solved by using ionic liquids as a trainer or cosolvent to supercritical CO₂ during the extraction process. The choice of ionic liquid over organic solvents used to enhance extraction yield and solubility is based on properties such as hydrophobicity, polarity and selectivity in addition to a safe environment.

Keywords: green extraction technology; value-added compounds; process industries; ionic liquids

1. Introduction

Recently, considerable emphasis has been placed on the reduction of carbon footprint for the development of smart cities worldwide. Chemical process industries can play an important role in achieving this objective by adopting technology which is environmentally sensitive using green solvents in separation and extraction processes, referred to as green technology. Green solvents and sustainable technologies are integrated into the extraction and separation of large numbers of bioactive products from biomass conversion. The new paradigm shift in the usage of bioactive products in multiple industries like pharmacy, food, refinery and textile suggests on one hand the acceptance of the need for healthy lifestyles and on the other hand, the need for chemical industries to use safe and appropriate techniques for extraction from biomass or fermentation broths [1–3]. In view of the foregoing, many green extraction and separation techniques including non-conventional as well as conventional methods...have been reported [4–6].

Nonconventional techniques including supercritical fluid extraction (SCFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), ultrasound extraction (UAE) and pulsed electric fields extraction (PEFE) have been reported in different process industries [1,7,8]. The above mentioned extraction methods are advantageous compared to conventional techniques [9]. Indeed, these techniques can operate without light and oxygen, at elevated temperature or pressure,

combined with low organic solvent consumption and extraction time. Long extraction time, high solvent cost, low selectivity and thermal decomposition of thermos-labile compounds are major challenges of conventional extraction [10]. These limitations can be removed using nonconventional extraction techniques.

The processing industry is regarded as one of the fastest growing sectors today with an estimated product growth rate of 8.6% per year [11]. The advancement in processing has been instrumental in the growth of pharmaceuticals, chemicals, food, textiles and refinery industries [12]. These industries are networks of equipment covering a number of combined technologies leading to the sustainable transformation of biomass for the concomitant production of biofuels, chemicals, natural products, food supplements or active compounds, preferably those which add value [13]. In this review, some of the nonconventional extraction techniques employed in processing industries are discussed and compared with the view to their merits and demerits, especially with respect to their application to a typical scale-up process and their economics. The view is to discuss the comparative advantage of high pressure technology with respect to SCFE methods especially as it applies to extraction or fractionation of biological/bioactive compounds and to highlight its comparative advantage when combined with ionic liquid as additional solvents to achieve more efficient extraction and fractionation.

2. Process Industries

Typical process industry raw material feedstocks are processed in a production plant which may consist of different unit operations working in continuous and/or batch mode. This definition is schematized in Figure 1, which explains the complex production chain that characterizes significant features with regard to products and processes developed in the processing industry. The greener nature plus high efficiency of nonconventional technologies have been shown to make them superior to conventional methods, especially with respect to product quality and integrity. While some industries still rely solely on the conventional technologies, the following section will discuss some selected nonconventional techniques used in the process industry that are relevant to refinery, food, health and textile. Details of these conventional technologies have been reviewed elsewhere [14]. Table 1 describes products that can be obtained from various feedstocks (raw materials) using nonconventional techniques reviewed in this paper in process industries with a focus on food and pharmaceutical industries. This shows that more interest has been given to food and pharmaceutical industries as compared to refinery, textile, and chemical industries using nonconventional techniques.

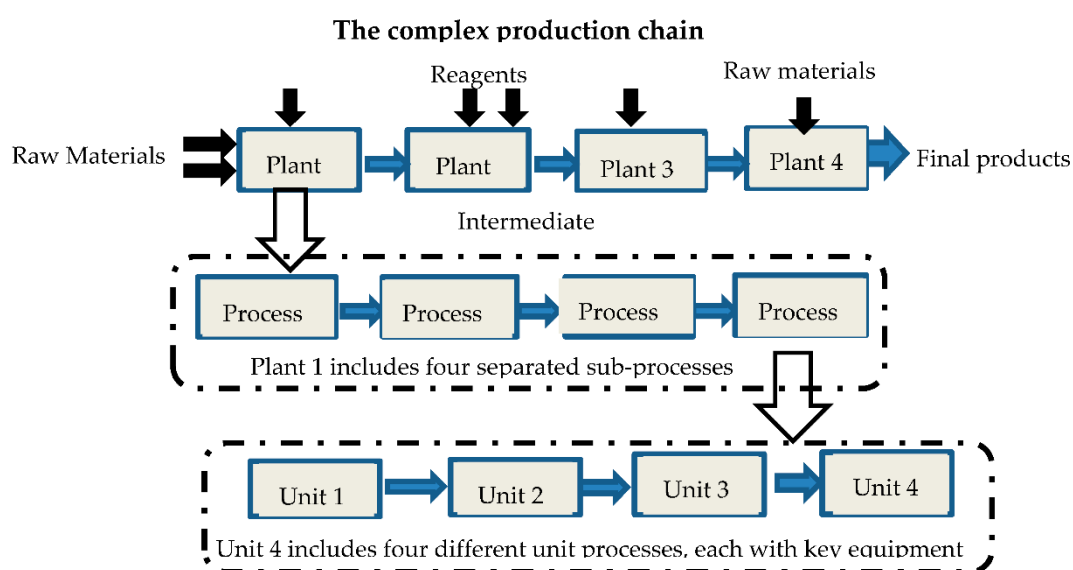


Figure 1. A schematic production process in industry.

Table 1. Some processing target ingredients and their sources in different industrial sectors reviewed in this work.

Industrial Sectors	Sources	Target Ingredients	Refs.
Refinery	- Oil sands, oil shale rock, lignite, tire, rubber	- Crude oil, diesel fuel, kerogen, hydrogen, methane	[15–17]
	- Tar sands	- Bitumen	[18]
	- Cannabis seeds	- Oil	[19]
	- Palm kernels	- Palm kernel oil	[20–22]
	- Heavy petroleum feedstocks	- Vanadium, nickel and iron	[23]
pharmaceutical	- Tinctures of sage, valerian	- Cineole, borneol, mixture of α - and β -thujones	[24]
	- Penggan (<i>Citrus reticulata</i>) peel	- Hesperidin	[25]
	- Grapes	- Tartaric acid	[26]
	- Vegetal sources	- Flavonoids	[27]
	- Bovine meat, porcine meat, poultry meat, sea bream fish, trout fish	- Antibiotics (Erythromycin A, Josamycin, Roxithromycin, Spiramycin, Tilmicosin, Troleandomycin, Tylosin)	[28]
	- Meat	- Tetracyclines (tetracycline, chlorotetracycline, oxytetracycline and doxycycline), sulfonamides	[29,30]
	-Sewage sludge	- Macrolides	[31]
	-Fish	- Paroxetine and fluoxetine	[32]
	- <i>Chlorella vulgaris</i>	- Carotenoid and chlorophylls	[33]
	- Soil	- Estrone (E1), 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2), estriol (E3)	[34,35]
	- Red pepper	- Vitamin E and provitamin A	[36]

Food	- olive leaves/fruit	-Sugars (polysaccharides), protein, fatty acids, pigments, and polyphenols, polyalcohols, lipids and pectins, tyrosol, hydroxybenzoic acid, cinnamic acid, hydroxytyrosol, caffeic acid, syringic acid, elenolic acid, chlorogenic acid, ligstroside, oleuropein, verbacoside, tocopherols, p-coumaric acid, vanillic acid, elenolic acid, catechol and rutin	[37–40]
	- Carrot, grapes, black tea, apple ginger	- Beta-carotene, polyphenol, tartaric acid, phenol, antioxidants, anthocyanins, polyphenol, aroma components, polyphenols, gingerol	[9,41,42]
	- Ginseng roots,	- Ginseng saponins	[43]
	- Caraway	- Caryone and limonene	[9]
	- <i>Amaranthus caudatus</i> seeds	- Vitamin E	[9]
	- Adlay seed	- (<i>Coix lachrymal-jobi</i> L. var. <i>Adlay</i>) oil and coixenolide	[44]
	- Egg yolk	- lutein	[45]
	- Garlic	- Essential oil: organo-sulfur compounds	[46,47]
	- Citrus Flowers and honey	- Linalool	[28]
	- Peppermint leaves	- Menthol	[48]
	- Tomatoes	- Carotenoids (all-trans-lycopene ,b-carotene)	[49]
	- Vegetal sources	- Phenolic acid, tannins, stilbenes	[50]
	- Crude palm oil and soybean oil	- Tocotrienols and tocopherols	[51]
	- Olive mill wastewater, sea buckborn, berry pomace, mango peel, white grape pomace	- Phenols	[52]
	- Soybean	- Isoflavones	[53]
	- Artichoke, blueberry, grapes and grape seeds, flaxseed hulls, orange peel, and tomato	- Phenolic compounds, flavonoids, anthocyanins, carotenoids	[54]
	- Orange juice and pasteurized juices	- Vitamin C	[55]
	- Fed cabbage	- Anthocyanin	[52]
	- Crude palm and soybean oil	- Tocotrienols and tocopherols	[56]

Textile	-Dye (turmeric, henna)	- Turmeric and henna extracts	[57]
	-Mordants (harda, tamarind seed coat)	- Harda and tamarind extracts	[58]
	- Red Beetroot (<i>Beta vulgaris</i>)	- Cyanins and betanin (red) and Betaxanthins. (Yellow)	[52]
	- Lac (<i>Kerria lacca</i>)	- Lacciac acid	[59]
	- <i>Dastylapius coccus</i> , <i>kermes liciis</i> , <i>kerria lacca</i> ,	- Cochineal (red), Kermes (red), lac	[60]
	-Artichoke, red cabbage, blueberry, grape seeds, flaxseed hulls, orange peel, tomato	- Phenolic compounds, flavonoids, anthocyanins, carotenoids	[51]
	- <i>Ricinus communis</i> leaves	-Natural dye	[61]
Chemical	- Grapes	-Tartaric acid	[35]
	- Corn starch or corn pericarp	-Carbohydrates (glucose, xylose and arabinose)	[62]

3. Nonconventional Extraction Methods in Process Industries

3.1. Ultrasound-Assisted Extraction (UAE)

UAE is a suitable, cost-effective, faster kinetic and efficient nonconventional technique in solid-liquid extraction operating at 20 kHz to 100 MHz, for heat sensitive compounds with minimal damage [63]. UAE technique is a relatively novel, environmentally friendly and economically viable alternative to conventional techniques applied in food, environmental, pharmaceutical, textile and chemical industries. The main improvement in works published on medicinal plant extraction using ultrasound is found to be efficiency and short time of extraction. Valachovic et al. [24] extracted tinctures of sage (*Salvia officinalis* L.) and valerian (*Valeriana officinalis* L.) with high antimicrobial activities using UAE at 20 kHz (600 W) for 6 h with ethanol/water. Yaqin Ma et al. produced hesperidin from Penggan (*Citrus reticulata*) peel at 60 kHz frequency and temperature of 40 °C for 1h in methanol [25]. In the pharmaceutical industry, the active zone and distribution of ultrasonic power are challenges that should be considered. The application of UAE technology in food processing is of interest to increase the extraction yield of polyphenolics, anthocyanins, aromatic compounds, polysaccharides and oils from plant and animal materials. Wu et al. [44] in 2001 and Chemat et al. [45] in 2004 used UAE at lower temperatures to extract ginseng saponins from ginseng roots, and caryone and limonene from caraway respectively. As egg yolk is an important source of lutein in some foods [64], Xiaohua et al. [43] extracted lutein from egg yolk by using sonication. From this study, it was found that depolymerization can lead to a decrease in the degree of acetylation which can limit this technique in food processing. Xiaohua et al. [43] obtained a large amount of lutein using UAE combined with saponificated organic solvent. Essential oil has been extracted from peppermint leaves [51], artemisia [65] and lavender [63] and from garlic [66] and citrus flowers [52] using UAE. For textile industry application, Sheikh et al. [55] extracted natural dyes (turmeric, henna) and mordants (harda, tamarind seed coat) for textile materials using UAE in water in comparison with conventional methods. Moreover, Kamel et al. [60] in 2004 studied the effect of pH, salt concentration, ultrasonic power and dyeing time during the extraction of laccic acid dye from lac (dye material of animal origin) in distilled water for dyeing wool fabric. Due to various mechanisms with cavitation in liquid, ultrasound has been beneficially applied in chemical processes. Presently, despite the limitation of UAE due to low efficiency and high operation costs, it is a promising extraction method for added-value pharmaceuticals, food and chemical ingredients on an industrial scale [67–71]. One of the challenges of UAE in the chemical industry is to obtain effective mass transfer with suitable mixing in order to create a strong interaction between the two immiscible phases.

3.2. Microwave-Assisted Extraction (MAE)

Microwaves are electromagnetic fields in the range of 300 MHz to 300 GHz. Microwave heating affects the frequency, power and speed, temperature, mass of food, water content, density, physical geometry, thermal properties, electrical conductivity and dielectric properties of molecules. No heating occurs when the frequency is less than 2450 MHz and the electrical component changes at a much lower speed. MAE is commonly used in organic and organometallic compound extraction; it utilizes water or alcohols as solvent at elevated temperatures and controlled pressure conditions [68]. However, for refinery application, numbers of reports have successfully investigated the extraction and separation of oil sands or oil shale. MAE was used to separate two samples of oil sands at 915 MHz, irradiated for 5 and 9 min at 500 W and 1500 W separately and reached final temperatures of 315 °C and 142 °C respectively [18]. These samples showed three distinct layers with the bottom layer mostly sand but also containing other solids; the second layer consisted of a yellowish solution, accounting for all the water and other impurities in the oil sand; and the top layer was black, viscous oil. Moreover, Bosisio et al. [72] used MAE to extract oil sands at room temperature in a quartz reactor with an incident microwave power of 100 W at 2450 MHz frequency. In addition, Balint et al. [73] described the irradiation of oil sand, oil shale rock and lignite samples in a pressure vessel with gaseous or liquefied carbon dioxide and other gaseous or vapor hydrocarbon solvents. In

pharmaceutical industry application, various studies have reviewed the use of MAE, some of which this work reviews. Ergosterol was produced from hyphae and spores using SCFE with lower yield compared with that of MAE [74]. Norproxifen materials as model medicines are the main applications in which the MAE technique is used. Carbamazepine, the most commonly employed pharmaceutical in the treatment of epilepsy and neuropathic pain, was recovered from wastewater sludge using MAE at 1200 W power and 110 °C for 10 min [75]. MAE has been effectively employed to produce many classes of antibiotics like levofloxacin, norfloxacin, ciprofloxacin, enrofloxacin, fluoroquinolones, tetracyclines from soil [76], sewage and wastewater sludge [77,78], compost [79] and aquifer sediments [74]. In the food industry, Koh et al. [80] investigated the recovery of pectin from jackfruit rinds at 90 °C at 450 W power for 10 min. On the other hand, the extraction of phenolic compounds from olive leaves and Melissa using MAE was reported by Rafiee et al. [81] and Ince et al. [82]. Rafiee et al. recovered phenolic compounds from olive leaves with different solvents at 15 min while Ince et al. focused on the extraction time and solid-to-solvent ratio for recovery of total phenolic compounds. Among the solvents used, ethanol was the most efficient where acetone was the least. In textile industry application, Sinha et al. [83] evaluated the effect of extraction time, pH of solution and the amount of pomegranate rind produced from brown dry rind of pomegranate using MAE for textiles. The effect of water and ethanol solvent at different temperatures with different material to solvent ratio and microwave power was studied for the extraction of natural tannins and flavonoid dyes from *coleus atropurpureus* leaves [58]. Raza et al. [84] extracted natural colorant for textile industry use from munj sweet cane by optimizing the temperature, time, fabric to extract ratio, salt type and salt concentration. In the chemical industry, few studies have been done on extraction using MAE. In 2010, Yoshida et al. [85] optimized the heating temperature, heating time and solid to liquid ratio when extracting carbohydrate compounds from corn pericarp with water as a solvent. In all the reviewed studies aforementioned, polarity or volatility of compounds/solvent may reduce the efficiency of the MAE, and more importantly, the high temperature requirement of this technology may preclude its application for extraction of thermolabile compounds such as can be found in bioactive materials and/or in compounds of pharmaceutical relevance. In addition, scaling of MAE system for industrial application is still in its infancy and largely limited to laboratory scale.

3.3. Pressurized Liquid Extraction (PLE)

Several bioactive compounds are extracted from different plants using PLE which is an alternative method used thanks to short time operation extraction (<30 min), inert environment under high pressure (<20 MPa) and temperatures (25–200 °C) and low solvent consumption [86]. This technique can be applied in different sectors like the pharmaceutical and food industries. In pharmaceutical application, Blasco et al. [87] evaluated the temperature, pressure, treatment of sand, static time, cell size, number of extraction cycles and flush volume for the extraction of four tetracyclines (tetracycline, chlorotetracycline, oxytetracycline and doxycycline) from different types of meat with water as solvent. Pharmaceutical compounds like estrogens are widely used products because of their contraceptive activity. Indeed, different works have reported on the production of estrogens such as estrone (E1), 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2) and estriol (E3) from soil using PLE [87]. Other studies investigated the extraction of other pharmaceutical compounds such as sulfonamides in meat [88] and paroxetine and fluoxetine in fish [31]. In addition, with regard to the food industry, Kwang et al. [89] optimized temperature and time to extract carotenoids and chlorophylls from the green microalga *Chlorella vulgaris* using PLE. On the other hand, reference [90] explored the extraction of polyphenols from the needles of *Pinus taiwanensis* and *Pinus morrisonicola* which involved enzymatic hydrolysis with a combination of many enzymes (cellulase, hemicellulase, pectinase and protease). Much interest has been given to essential oils from herbal plants in the food, pharmaceutical and cosmetic industries due to their antimicrobial, antioxidant and antifungal activities, aroma-active constituents and flavor properties [91–93].

3.4. Pulsed Electric Fields Extraction (PEFE)

The principle of PEFE is to induce the electroporation of the cell membrane, thereby increasing the extraction yield. The pulse amplitude ranges from 100 to 300 V/cm to 20 to 80 kV/cm. Solvent as water and agri-solvents (ethanol and methyl esters of fatty acids from vegetable oils) are used in PEFE, hence this technique is considered a green extraction technique producing extracts of high quality and purity [94]. PEFE is mostly applied in food preservative from plant food materials, food wastes and byproducts [95,96]. This technique can be applied in the biorefinery, pharmaceutical and food industries. In the biorefinery industry, the extraction of intracellular compounds is the most interesting feature of PEF treatment. For example, the extraction of sucrose from sugar beet, colorants from grapes and red beet, polyphenols from green biomass and lipids from microalgae use the pulsed electric fields method [97]. Haji-Moradkhani et al. [19] evaluated the speed of pulsing oil on the physicochemical properties of cannabis oil extracted from cannabis seeds. Leong et al. [98] produced anthocyanins from grape juice after PEF treatment at 20 mS pulse with 50 Hz under an electric field strength of 1.5 kV/cm. This technique was shown to be efficient by providing pure extracts with the ability to protect cells from oxidative stress. Moubarik et al. [99] reported that fennel (*Foeniculum vulgare*) extracts with valuable antioxidants and medicinal properties have also been obtained using PEFE and the extraction yield was enhanced. PEF treatment applied to artichoke, blueberry, grapes and grape seeds, flaxseed hulls, orange peel and tomato enhance the yield of phenolic acid, flavonoids, anthocyanins and carotenoid compounds [52]. The extraction of polyphenols and flavonoid derivatives from orange peel using PEFE has been reported [48]. Moreover, Segovia et al. [100] investigated the isolation of polyphenols from *Borago officinalis* leaves using PEF treatment. The polyphenol and oxygen radical absorption capacity (ORAC) values were increased between 1.3% and 6.6% and from 2.0% to 13.7%, respectively. Jaeger et al. [101] used the PEF technique for extraction of apple juice. Elez-Martinez and Martín-Belloso extracted vitamin C from orange juice and the content of vitamin C was compared with that in conventionally pasteurized juices which showed higher content in PEF-treated orange juice than in pasteurized juice [54].

3.5. Supercritical CO₂ (SC-CO₂) Extraction

Supercritical extraction is based on the change in temperature and pressure which transform the gas used in supercritical fluid. Supercritical fluid (SCF) is fluid whose temperature and pressure values are above the critical temperature (T_c) and critical pressure (P_c) values. T_c and P_c values are different for each supercritical fluid. CO₂, N₂O, NH₃, H₂O, CHF₃ and SF₆ compounds have been considered as supercritical fluids in the SCF process [102,103]. For example, T_c and P_c values for these supercritical fluids are presented in Table 2. CO₂ is the most commonly used SCF because of its low critical temperature and nonexplosive character; it is safe and inexpensive and has important qualities for pharmaceutical application. Controlled increase in temperature and pressure values brings these two parameters together at a common point called the “critical point.” Thus, T_c and P_c values are the temperature and pressure values possessed at the critical point (see Figure 2). When this point is reached, the solvent is described as SCF.

Table 2. Critical conditions of some fluids used in supercritical fluid (SCF) extraction and separation.

	CO ₂	H ₂ O	N ₂ O	CHF ₃	SF ₆	NH ₃
T _c (K)	304.2	646.8	309.6	299.1	318.7	405.59
P _c (MPa)	7.37	22.06	7.24	4.83	3.76	11.28

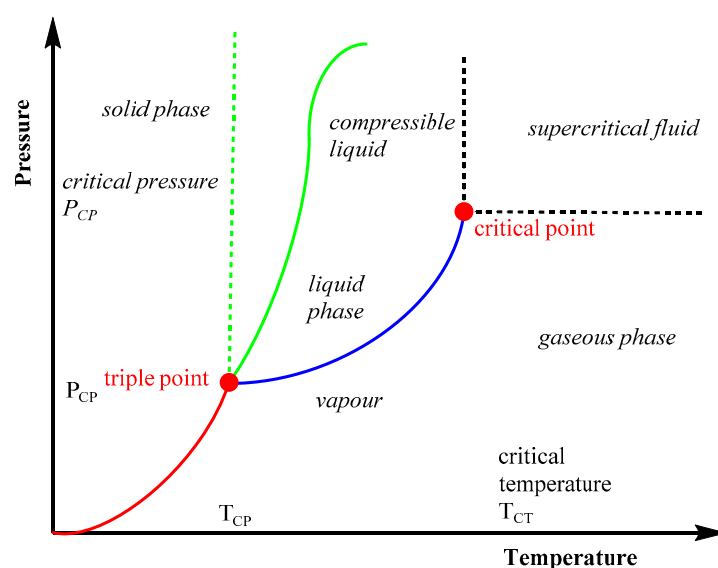


Figure 2. Diagram of critical temperature, pressure and critical point.

Supercritical CO₂ (SC-CO₂) extraction has been applied in various sectors such as the food, chemical and pharmaceutical industries [104,105]. The main limitation remains its high cost and the difficulty of performing continuous extractions [106]. The SC-CO₂ process in the oil refinery industry is used to deasphalt the oil and heavy residues by reducing the solvent ratio when removing raw materials and improving the efficiency of the process. Magomedov et al. [23] investigated the demetallization of heavy petroleum feedstocks (HPF) using SFE for the extraction of vanadium, nickel and iron. In addition, many other researchers have investigated the extraction and fractionation of palm kernel oil from palm kernels using SCFE [19–22]. The yield of palm kernel oil was shown to increase with pressure (34.5 to 48.3 MPa at 353.2 K). At lower pressure (20.7 to 27.6 MPa), lower amounts of shorter chain triglycerides (C8–C14) were obtained. Fatty acid constituents with long chain (C16–C18) were extracted at higher pressures from 34.5 to 48.3 MPa. At higher temperature, the extracted palm kernel oil was found to be superior in terms of the constituent of fatty acids in triglycerides compared to that obtained from Soxhlet extraction using hexane. Pharmaceutical/cosmetic active compounds can be obtained from either natural or synthetic and polymeric patches or implants and cosmetic lacquers using the SCF process. Romo-Hualde et al. [107] in 2012 evaluated various parameters that can affect the extraction yield using CO₂ as the supercritical fluid. These authors found that the highest yield of vitamin E (97%) and provitamin A (68.1%) in red pepper (*Capsicum annum* L.) can be obtained at a temperature of 60 °C at 24 Pa and using a particle size of 0.2–0.5 mm. In food applications, many important food ingredients from the health point of view have been extracted using SC-CO₂ process by many researchers [108]. Products produced by SCF technology such as flavored orange juice, vitamin additives, dealcoholized wine/beer, defatted meat, defatted potato chips and spice extracts are commonly found on our tables [109]. Moreover, Guedes et al. [110] used supercritical fluid to produce carotenoids and a, b and c chlorophylls from *Microalga Scenedesmus obliquus* for subsequent use in food processing. The highest yields were obtained at 250 bars. The most suitable temperature to obtain the highest yield for chlorophyll was 40 °C and for carotenoids was 60 °C. The supercritical fluid process is also used in the refinery industry for food ingredient production such as colorants, antioxidant preservatives, texture agents and low-fat products. In the textile industry, the phase behavior of the system consisting of solids and gas should be well described when working with supercritical systems in dyeing [111]. Saus et al. [111] reported in situ results on the dyeing of poly (ethylene terephthalate) and other synthetic materials with factors influencing dye uptake and levelness. In addition, Sanchez-Sanchez et al. [112] impregnated a polyester textile with mango leaf extracts (MLE) in the mixture of CO₂/methanol (50%) at 120 bar and 100 °C and the extracts presented antioxidant, bacteriostatic and bactericidal activities. SCFs are used in some chemical reactions (ammonolysis, alkylation, polymerization, field crafts,

hydroformylation, hydrogenation, inorganic catalytic processes, metathesis and oxidation) that have already been implemented at industrial scale to obtain added-value products [113]. Examples are the ammonolysis reaction of ester to amides in supercritical ammonia, the asymmetric hydrogenation in SC-CO₂ and also the synthesis of D, L- α Tocopherol in SC-CO₂ and in SC-N₂O [114]. In addition, the hydrogenation reaction of organic compounds in SCFs was implemented at industrial scale [115] by Thomas Swan and Co Ltd Company in 2000.

4. Comparison of SCFE with Other Extraction Methods

Table 3 compares the green extraction methods considered in this review in terms of their operational conditions. Unlike SCFE (that uses SC-CO₂), all these techniques in addition to water, ethanol and methanol use other organic solvents which compromise the greener nature of the technique. When comparing energy consumption, SCFE process requires less energy than other techniques. These make SCFE more economically suitable for research and industrial applications. Even though UAE, MAE, PLE and PEFE methods are widely applied in extraction fractionation and separation processes, they present certain limitations such as high energy costs, low selectivity and large quantities of solvent waste [116] which is not the case with SCFE. Besides that, MAE and PLE techniques are not suitable for thermolabile compounds due to high temperature applied; the advantage of the SCF CO₂ process is that it does not destroy thermolabile compounds at critical temperature and pressure. Despite all the advantages of SCFE, this technique also has certain limitations when extracting or fractionating separating polar compounds which are due to the nonpolar character of CO₂. However, many researchers have shown that the use of a polar solvent as modifier or cosolvent will overcome the challenge [117].

Table 3. Summary of nonconventional (green) extraction methods considered in this review.

Conditions	UAE	MAE	PLE	PEFE	SCFE	Comments
Extraction solvent	Hexane, water, Dichloro-methane, Acetone, ethanol	Hexane, water, Dichloro-methane, Acetone, ethanol	H ₂ O/EtOH, Ethanol	EtOAc/MeOH/H ₂ O, CO ₂ /MeOH, olive oil	SC-CO ₂ , SC-CO ₂ /MeOH SC-CO ₂ /EtOH	• CO₂ suitable for bioactive compounds • CO₂ density CO₂ can be controlled • CO₂ has low viscosity and high diffusivity • MAE requires large solvent volume • In SCFE, CO₂ has difficulty in dissolving compounds with high molar mass like carotenoids, triacyl-glycerides....
Extraction temperature	10–70 °C	80–350 °C	50–190 °C	<100 °C	30–100 °C	• MAE is applied at elevated temperatures • PLE, MAE not suitable for thermos labile compounds • With SCFE, low critical temperature and low reactivity of CO₂. • SFE performed at low temperatures, ideal for thermally labile compounds
Extraction time	10–90 min	3–30 min	<1 h	<1 h	10–60 min	• with SCFE, few tens of minutes for extraction time • MAE has the limitations of requiring longer extraction time
Power Amount	48–600 W	180–1200 W	Moderate	30 kW	Moderate	• In SFE, changing pressure/temperature changes solvation power leading to high selectivity
Cost effective	High cost	Low cost	Low cost	Low cost	Relatively low	• SCFE: operating cost (cleaning and maintenance) underestimated • PEFE, the electricity cost about \$0.33 per metric ton • PLE, high manufacturing cost US\$29.2/kg extract compared to PEFE - For MAE, low production cost
Industrial sectors	- Food - Pharmaceutica - Chemical - Textile	- Refinery - Food - Pharmaceutical - Chemical - Textile	- Food - Pharmaceutical	- Refinery - Food - Pharmaceutical	- Refinery - Food - Pharmaceutical - Chemical	• UAE, MAE, promising in pharmaceutical, food and chemical industries • MAE, mostly applied in refinery, pharmaceutical and textile industries • PLE widely applied in food and pharmaceutical industry • PEFE applied in food and pharmaceutical - SCFE widely used in food, textile, refinery, pharmaceutical and chemical industries

The addition of polar solvents such as acetone, *n*-heptane, toluene or mixtures of toluene and *n*-heptane with acetone and ethanol, methanol, ethanol, acetonitrile, ethyl acetate, toluene and *o*-xylene have been used to increase the solvent power of supercritical fluids [118]. Even though these polar solvents improve the extraction yield and the viscosity of the CO₂, they compromise the green qualities of SCF technology. Therefore, the alternative way to increase the polarity of the CO₂, yield of extraction and extraction time without affecting the environmentally friendly nature of this SC-CO₂ technique could be the use of ionic liquids as cosolvents or modifiers. A number of theoretical and experimental works have already been reported to prove the concept of ionic liquids in green extraction and separation technology (MAE, UAE, PLE, PEFE) in processing or bioprocessing industries [119,120]. However, the application of ionic liquids as cosolvents or entrainers or modifiers for the extraction and recovering of various compounds with high concentration using SC-CO₂ technique is rare. As presented in some studies, ionic liquids are 100% soluble in SC-CO₂ so the recovery of value-added compounds using SCFE with ionic liquids as modifier will be very easy.

5. Ionic Liquids as Green Solvent

Ionic liquids (ILs) are liquid salts at temperatures <100 °C, [121], constituted of asymmetrical organic cations, organic or inorganic anions and are described as solvents designed with adjustable properties such as thermophysical, biodegradability, toxicity and hydrophobicity features [122]. Many protic and aprotic ILs such as ethylammonium nitrate, (C₂H₅)NH₃⁺·NO₃[−] and 1-butyl-3-methylimidazolium have been synthesized since 1914 [123,124]. More attention has been given to aprotic ILs for their excellent properties such as thermal stability over a broad temperature range, electrochemical stability, nonflammability and low volatility and high ionic conductivity [125]. These properties make them potentially effective solvent materials for organic synthesis, extraction and separation processes, catalysis, electrochemistry and also as a good stabilizing agent for proteins, enzymes and nucleic acids [126]. The thermal stability, solubility and viscosity which are essential properties of ILs for their application in supercritical fluid extraction and separation of bioactive added-value compounds recovered from biomass have been well investigated in a number of works [127,128]. In addition, the lack or extremely low vapor pressure of ILs at room temperature is a very significant feature leading to their categorization as green solvents, and this feature has been explored in many applications [129,130].

5.1. Ionic Liquid/SC-CO₂ Extraction or Fractionation

Much research focusing on ILs has reported on their application in chemical and processing industries; however, their suitability in SCF processes may be attributed to their thermal stability, solubility and viscosity. Their application in the recovery of added-value compounds from biomass material has been well investigated and studied in a number of published works [131,132]. The ILs/SC-CO₂ system is relatively new and unexplored at least in process industries. The mechanism is such that organic salts in liquid form interact selectively with polar and nonpolar compounds using π -stacking interactions, hydrogen bonding, ion exchange and hydrophobic interactions, and due to the ionic interactions, the quality and efficiency of the extraction is very high [133]. In metallurgical application, Mekki et al. [134] extracted trivalent lanthanum and europium from nitric acid solution using a three-step extraction system of water/ionic liquid/SC-CO₂. This work used the imidazolium-based (1-butyl-3-methylimidazolium (BMIM)) ionic liquid, with bis(trifluoromethylsulfonyl)-imide (Tf₂N[−]=(CF₃SO₂)₂N[−]) as counter anions with low complexing abilities. Shaofen Wang et al. [135] on the other hand extracted uranyl ions [UO₂]²⁺ from nitric acid solution with imidazolium-based ionic liquid with tri-*n*-butyl phosphate using SC-CO₂. The uranyl complex recovered in the SC-CO₂ phase was identified to be [UO₂(NO₃)₂·(TBP)₂]. Figure 3 shows the schematic diagram of the two biphasic system for extraction process. From the literature up to date, no work has been reported using an IL/SC-CO₂ mixture for extraction of bioactive products in refinery, pharmaceutical, food, textile and chemical industries. However, from work done in these industrial sectors using other green techniques than SCF, with VLE data and phase behavior of IL/SC-CO₂ physical and critical properties and with IL/SC-CO₂ interaction studies [136], we can therefore say in this review that the extraction

or fractionation of value-added products using IL/SC-CO₂ mixture in high pressure technology is possible.

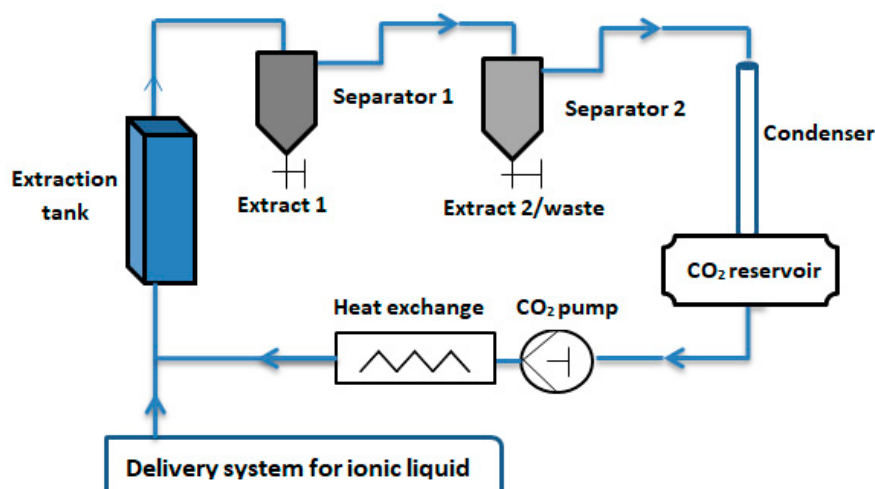


Figure 3. A simplified drawing of a process-scale IL/SC-CO₂ extractor.

5.2. Extract Recovery from ILs with SC-CO₂ Process

The application of SC-CO₂ for recovering of products from ionic liquids relies principally on its solubility/phase behavior in the binary IL/CO₂ system. From the literature, behaviors of the IL/CO₂ system are different from other organic liquid/CO₂ systems. As an example, Blanchard et al. [137] studied the qualitative phase behavior of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆])/CO₂ system within a wide pressure range. They studied the ([bmim][PF₆])/CO₂ system phase behavior at 3100 bar and found two different phases. The two distinct phases were explained by the fact that at high-pressure density of pure CO₂, vapor phase increases but since the liquid phase does not expand, the two phases will never become identical. Therefore, the IL/CO₂ system remains as two phases even at very high pressure; although the CO₂ solubility is quite high, the mixture will never become a single phase. Blanchard et al. in 2001 [137] showed that CO₂ dissolves in the liquid phase of ILs while the IL remains insoluble in the CO₂ vapor phase. In addition, Kroon et al. [138] experimentally studied the recovery of *N*-acetyl-(S)-phenylalanine methyl ester (APAM) from the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) using SC-CO₂ as a cosolvent in extractions or as an antisolvent in precipitation [139]. These authors found that solubility of this APAM was lower in ionic liquid/SC-CO₂ mixture compared to the one in pure ionic liquid at room temperature and the extracted product has no trace of ionic liquid. Table 4 presents some ILs and their properties reported in literature used in SC-CO₂. Among the listed ILs, 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide [C4mim][Tf₂N] has high thermal stability at 450.2 °C and density of 1.4099 g·cm⁻³ (at 25 °C with least viscosity of 44 (25 °C) MPa.s. The IL 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C8-mim][PF₆]) is the most soluble in CO₂ at 60 °C with high viscosity of 866 at 20 °C.

Table 4. Properties and characteristics of ionic liquids used with supercritical CO₂ for extraction and separation purposes.

Ionic Liquids	Thermal Stability/°C	Solubility in CO ₂	Viscosity/MPa.s	Density/g·cm ⁻³
1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF ₆])	410 [140]	0.231 (40 °C, 14.17 bar); 0.236 (50 °C, 17.38 bar) 0.228 (60 °C, 15.79) [141]	707 (293.15 K, 0.1 MPa) [142]	1.345 (1 MPa, 323.15 K) [143]
1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF ₄])	372.73 [143]	-	122.35 [144]	1.1647 [145]
1- <i>n</i> -octyl-3-methylimidazolium hexafluorophosphate ([C8-mim][PF ₆])	-	0.234 (40 °C, 17.93 bar) 0.223 (50 °C, 16.00 bar) 0.248 (60 °C, 17.38 bar) [141]	866 (20 °C)	1.211 (40 °C); 1.204 (50 °C); 1.197 (60 °C) [141]
1- <i>n</i> -octyl-3-methylimidazolium tetrafluoroborate ([C8-mim][BF ₄])	397 [144]	0.197 (40 °C, 17.26 bar) 0.191 (50 °C, 15.61 bar) 0.160 (60 °C, 15.61 bar) [141]	439 (20 °C) [146]	1.080 (40 °C); 1.073 (50 °C); 1.066 (60 °C) [141]
1- <i>n</i> -butyl-3-methylimidazolium nitrate ([bmim][NO ₃])	297.49 [145]	0.196 (40 °C, 15.47 bar) 0.169 (50 °C, 17.12 bar) 0.183 (60 °C, 18.37bar) [141]	450.43 (283.15 K) [147]	1.149 (40 °C); 1.143 (50 °C); 1.136 (60 °C) [141]
1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO ₄])	-	0.100 (40 °C, 16.43 bar) 0.103 (50 °C, 16.22 bar) 0.118 (60 °C, 14.36 bar) [141]	97.2 (298.16 K) [148]	1.225 (40 °C); 1.218 (50 °C); 1.213 (60 °C) [141]
<i>N</i> -butylpyridinium tetrafluoroborate ([N-bupy][BF ₄])	373 [146]	0.144 (40 °C, 15.47bar) 0.142 (50 °C, 16.57 bar) 0.166 (60 °C, 18.65 bar) [141]	163.26 (298.15 K) [149]	1.203 (40 °C); 1.197 (50 °C); 1.190 (60 °C) [141]
1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide [C4mim][Tf ₂ N]	450.2 [150]	-	44 (25 °C) [145]	1.409 9 (25 °C) [150]

6. Conclusions

The significant potential of nonconventional methods as extraction and separation techniques for high-added value compounds from biomass or synthetic processes or fermentation broths in many process industries is increasingly being reviewed. The novel extraction technologies reviewed in this paper have the potential to significantly enhance the extraction yield. However, the maximum benefits of SCFE can be achieved only if a limitation regarding low concentration of compounds with high polarity and molecular weight is overcome. This review thus presented the introduction of ionic liquids as cosolvent in supercritical CO₂ extraction to overcome this limitation. Another promising technology recently reported that was not reviewed in this paper consists of gas assisted mechanical expression (GAME) which has shown interesting results on oil extraction from vegetable matrices. Future research priorities in the area of high pressure processing technology should concentrate on the use of ionic liquids as cosolvent as this has been proved to work in industrial scale for extraction/separation of high-added value compounds.

Author Contributions: G.F. hosting by T.V.O. and T.N.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Cape Peninsula University of Technology of the Republic of South Africa.

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

References

1. Azmir, J.; Zaidul, I.; Rahman, M.M.; Sharif, K.; Mohamed, A.; Sahena, F.; Jahurul, M.; Ghafoor, K.; Norulaini, N.; Omar, A. Techniques for extraction of bioactive compounds from plant materials: A review. *J. Food Eng.* **2013**, *117*, 426–436, doi:10.1016/j.jfoodeng.2013.01.014.
2. Bandar, H.; Hijazi, A.; Rammal, H.; Hachem, A.; Saad, Z.; Badran, B. Techniques for the extraction of bioactive compounds from *Lebanese urtica dioica*. *AJPCT* **2003**, *1*, 507–513.
3. Güvenç, A.; Mehmetoğlu, Ü.; Çalımlı, A. Extraction of ethanol from fermentation broth using supercritical CO₂. *Process Techn. Proc.* **1996**, *12*, 463–468, doi:10.1016/S0921-8610(96)80080-X.
4. Dai, J.-Y.; Sun, Y.; Xiu, Z.-L. Separation of bio-based chemicals from fermentation broths by salting-out extraction. *Eng. Life Sci.* **2014**, *14*, 108–117, doi:10.1002/elsc.201200210.
5. Baghdikian, B.; Filly, A.; Fabiano-Tixier, A.-S.; Petitcolas, E.; Mabrouki, F.; Chemat, F.; Ollivier, E. Extraction by solvent using microwave and ultrasound-assisted techniques followed by HPLC analysis of Harpagoside from *Harpagophytum procumbens* and comparison with conventional solvent extraction methods. *Comptes Rendus Chim.* **2016**, *19*, 692–698, doi:10.1016/j.crci.2016.02.020.
6. Barba, F.; Grimi, N.; Vorobiev, E. New Approaches for the Use of Non-conventional Cell Disruption Technologies to Extract Potential Food Additives and Nutraceuticals from Microalgae. *Food Eng. Rev.* **2014**, *7*, 45–62, doi:10.1007/s12393-014-9095-6.
7. Kadam, S.; Tiwari, B.K.; O'Donnell, C.J. Application of Novel Extraction Technologies for Bioactives from Marine Algae. *J. Agric. Food Chem.* **2013**, *61*, 4667–4675, doi:10.1021/jf400819p.
8. Hrncić, M.K.; Cör, D.; Verboten, M.T.; Knez, Ž. Application of supercritical and subcritical fluids in food processing. *Food Qual. Saf.* **2018**, *2*, 59–67, doi:10.1093/fqsafe/fyy008.
9. Wu, J.; Lin, L.; Chau, F. Ultrasound-assisted extraction of ginseng saponins from ginseng roots and cultured ginseng cells. *Ultrason Sonochem.* **2001**, *8*, 347–352.
10. De Castro, M.L.; García-Ayuso, L.E. Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. *Anal. Chim. Acta* **1998**, *369*, 1–10, doi:10.1016/S0003-2670(98)00233-5.
11. Ade, N.; Koirala, Y.; Mannan, M.S. Towards an inherently safer bioprocessing industry: A review. *J. Loss Prev. Process. Ind.* **2019**, *60*, 125–132, doi:10.1016/j.jlp.2019.04.015.
12. Chen, G.-Q. New challenges and opportunities for industrial biotechnology. *Microb. Cell Factories* **2012**, *11*, 111, doi:10.1186/1475-2859-11-111.
13. Morais, A.R.C.; Lukasik, R.M. Green chemistry and the biorefinery concept. *Sustain. Chem. Process.* **2013**, *1*, 18, doi:10.1186/2043-7129-1-18.

14. Chemat, F.; Fabiano-Tixier, A.S.; Vian, M.A.; Allaf, T.; Vorobiev, E. Solvent-free extraction of food and natural products. *TrAC Trends Anal. Chem.* **2015**, *71*, 157–168, doi:10.1016/j.trac.2015.02.021.
15. Dumbaugh, W.H.; Lawless, W.N.; Malmendier, J.W.; Wexell, D.R. Extraction of oil from oil shale and tar sand, Canadian Patent, 1108081, **2001**.
16. Pingle, F.G. Microwave based recovery of hydrocarbons and fossil fuels, U.S. Patent application No. 11/610,823, **2006**.
17. Pierre, E.P. Microwave Separation of Bituminous Material from tar Sands. Canadian Patent No 1293943, 1992.
18. Haji-Moradkhani, A.; Rezaei, R.; Moghimi, M. Optimization of pulsed electric field-assisted oil extraction from cannabis seeds. *J. Food Process. Eng.* **2019**, *42*, e13028, doi:10.1111/jfpe.13028.
19. Zaidul, I.; Norulaini, N.N.; Omar, A.M.; Smith, R.L. Supercritical carbon dioxide (SC-CO₂) extraction of palm kernel oil from palm kernel. *J. Food Eng.* **2007**, *79*, 1007–1014, doi:10.1016/j.jfoodeng.2006.03.021.
20. Norulaini, N.N.; Zaidul, I.M.; Anuar, O.; Ab Kadir, M.O. Supercritical enhancement for separation of lauric acid and oleic acid in palm kernel oil (PKO). *Sep. Purif. Technol.* **2004**, *35*, 55–60, doi:10.1016/s1383-5866(03)00130-8.
21. Norulaini, N.A.N.; Zaidul, I.S.M.; Anuar, O.; Azlan, A.; Ab Kadir, M.O. Supercritical Reduction of Lauric Acid in Palm Kernel Oil (PKO) to Produce Cocoa Butter Equivalent (CBE) Fat. *J. Chem. Eng. Jpn.* **2004**, *37*, 194–203, doi:10.1252/jcej.37.194.
22. Hassan, M.; Rahman, N.; Ibrahim, M.H.; Ab Kadir, M.O. Simple fractionation through the supercritical carbon dioxide extraction of palm kernel oil. *Sep. Purif. Technol.* **2000**, *19*, 113–120, doi:10.1016/s1383-5866(99)00082-9.
23. Magomedov, R.; Pripakhaylo, A.V.; Maryutina, T.A. Solvent demetallization of heavy petroleum feedstock using supercritical carbon dioxide with modifiers. *J. Supercrit. Fluids* **2017**, *119*, 150–158, doi:10.1016/j.supflu.2016.08.022.
24. Valachovic, P.; Pechova, A.; Mason, T.J. Towards the industrial production of medicinal tincture by ultrasound assisted extraction. *Ultrason. Sonochemistry* **2001**, *8*, 111–117, doi:10.1016/s1350-4177(00)00066-3.
25. Ma, Y.; Ye, X.; Hao, Y.; Xu, G.; Xu, G.; Liu, D. Ultrasound-assisted extraction of hesperidin from Penggan (*Citrus reticulata*) peel. *Ultrason. Sonochemistry* **2008**, *15*, 227–232, doi:10.1016/j.ultsonch.2007.03.006.
26. Vilku, K.; Mawson, R.; Simons, L.; Bates, D. Applications and opportunities for ultrasound assisted extraction in the food industry—A review. *Innov. Food Sci. Emerg. Technol.* **2008**, *9*, 161–169, doi:10.1016/j.ifset.2007.04.014.
27. López, N.P.; Ayora-Talavera, T.D.R.; Espinosa-Andrews, H.; Sanchez-Contreras, A.; Pacheco, N. Ultrasound Assisted Extraction for the Recovery of Phenolic Compounds from Vegetable Sources. *Agronomy* **2017**, *7*, 47.
28. Berrada, H.; Borrull, F.; Font, G.; Marcé, R.M. Determination of macrolide antibiotics in meat and fish using pressurized liquid extraction and liquid chromatography–mass spectrometry. *J. Chromatogr. A* **2008**, *1208*, 83–89, doi:10.1016/j.chroma.2008.08.107.
29. Blasco, C.; Di Corcia, A.; Pico, Y. Estrogens produced such as estrone (E1), 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2), estriol (E3) from soil using PLE. *Food Chem.* **2009**, *116*, 1005.
30. Chu, S.; Metcalfe, C.D. Analysis of paroxetine, fluoxetine and norfluoxetine in fish tissues using pressurized liquid extraction, mixed mode solid phase extraction cleanup and liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* **2007**, *1163*, 112–118, doi:10.1016/j.chroma.2007.06.014.
31. Göbel, A.; Thomsen, A.; Mc Ardell, C.S.; Alder, A.C.; Giger, W.; Theiß, N.; Löffler, D.; Ternes, T.A. Extraction and determination of sulfonamides, macrolides, and trimethoprim in sewage sludge. *J. Chromatogr. A* **2005**, *1085*, 179–189, doi.org/10.1016/j.chroma.2005.05.051.
32. Beck, J.; Totsche, K.U.; Kögel-Knabner, I. A rapid and efficient determination of natural estrogens in soils by pressurised liquid extraction and gas chromatography–mass spectrometry. *Chemosphere* **2008**, *71*, 954–960, doi:10.1016/j.chemosphere.2007.11.062.
33. Petrovic, M.; Viana, P.; Cespedes, R.; Raldúa, D.; Saura, Úrsula; Piña, B.; Lacorte, S.; Barceló, J. Integrated procedure for determination of endocrine-disrupting activity in surface waters and sediments by use of the biological technique recombinant yeast assay and chemical analysis by LC-ESI-MS. *Anal. Bioanal. Chem.* **2004**, *378*, 697–708, doi:10.1007/s00216-003-2303-5.

34. Dussault, È.B.; Balakrishnan, V.K.; Solomon, K.R.; Sibley, P. Matrix effects on mass spectrometric determinations of four pharmaceuticals and personal care products in water, sediments, and biota. *Can. J. Chem.* **2009**, *87*, 662–672, doi:10.1139/v09-042.
35. Ghanbari, R.; Anwar, F.; Alkharfy, K.M.; Gilani, A.-H.; Saari, N. Valuable Nutrients and Functional Bioactives in Different Parts of Olive (*Olea europaea* L.)—A Review. *Int. J. Mol. Sci.* **2012**, *13*, 3291–3340, doi:10.3390/ijms13033291.
36. Rigane, G.; Bouaziz, M.; Baccar, N.; Abidi, S.; Sayadi, S.; Ben Salem, R. Recovery of Hydroxytyrosol Rich Extract from Two-Phase Chemlali Olive Pomace by Chemical Treatment. *J. Food Sci.* **2012**, *77*, C1077–C1083, doi:10.1111/j.1750-3841.2012.02898.x.
37. Uribe, E.; Lemus-Mondaca, R.; Vega-Gálvez, A.; López, L.A.; Pereira, K.; López, J.; Ah-Hen, K.S.; Di Scala, K. Quality Characterization of Waste Olive Cake During Hot Air Drying: Nutritional Aspects and Antioxidant Activity. *Food Bioprocess Technol.* **2012**, *6*, 1207–1217, doi:10.1007/s11947-012-0802-0.
38. Roselló-Soto, E.; Koubaa, M.; Moubarik, A.; Lopes, R.; Saraiva, J.A.; Boussetta, N.; Grimi, N.; Barba, F. Emerging opportunities for the effective valorization of wastes and by-products generated during olive oil production process: Non-conventional methods for the recovery of high-added value compounds. *Trends Food Sci. Technol.* **2015**, *45*, 296–310, doi:10.1016/j.tifs.2015.07.003.
39. Xia, T.; Shi, S.; Wan, X. Impact of ultrasonic-assisted extraction on the chemical and sensory quality of tea infusion. *J. Food Eng.* **2006**, *74*, 557–560, doi:10.1016/j.jfoodeng.2005.03.043.
40. Ghafoor, K.; Choi, Y.H.; Jeon, J.Y.; Jo, I.H. Optimization of Ultrasound-Assisted Extraction of Phenolic Compounds, Antioxidants, and Anthocyanins from Grape (*Vitis vinifera*) Seeds. *J. Agric. Food Chem.* **2009**, *57*, 4988–4994, doi:10.1021/jf9001439.
41. Bruni, R.; Guerrini, A.; Scalia, S.; Romagnoli, C.; Sacchetti, G. Rapid techniques for the extraction of vitamin E isomers from *Amaranthus caudatus* seeds: ultrasonic and supercritical fluid extraction. *Phytochem. Anal.* **2002**, *13*, 257–261, doi:10.1002/pca.651.
42. Hu, A.-J.; Zhao, S.; Liang, H.; Qiu, T.-Q.; Chen, G. Ultrasound assisted supercritical fluid extraction of oil and coixenolide from adlay seed. *Ultrason. Sonochemistry* **2007**, *14*, 219–224, doi:10.1016/j.ultsonch.2006.03.005.
43. Yue, X.; Xu, Z.; Prinyawiwatukul, W.; King, J.M. Improving Extraction of Lutein from Egg Yolk Using an Ultrasound-Assisted Solvent Method. *J. Food Sci.* **2006**, *71*, C239–C241, doi:10.1111/j.1750-3841.2006.00027.x.
44. Alissandrakis, E. Ultrasound-assisted extraction of volatile compounds from citrus flowers and citrus honey. *Food Chem.* **2003**, *82*, 575–582, doi:10.1016/s0308-8146(03)00013-x.
45. Shotipruk, A.; Kaufman, P.; Wang, H.Y. Feasibility Study of Repeated Harvesting of Menthol from Biologically Viable *Mentha x piperata* Using Ultrasonic Extraction. *Biotechnol. Prog.* **2001**, *17*, 924–928, doi:10.1021/bp010074u.
46. Zhang, L.; Zelong, L. Optimization and comparison of ultrasound/microwave assisted extraction (UMAE) and ultrasonic assisted extraction (UAE) of lycopene from tomatoes. *Ultrason. Sonochemistry* **2008**, *15*, 731–737, doi:10.1016/j.ultsonch.2007.12.001.
47. Luengo, E.; Condón-Abanto, S.; Condón, S.; Álvarez, I.; Raso, J. Improving the extraction of carotenoids from tomato waste by application of ultrasound under pressure. *Sep. Purif. Technol.* **2014**, *136*, 130–136, doi:10.1016/j.seppur.2014.09.008.
48. Jungfer, M. Gegenstromtrennung Von Schwerflüchtigen Naturstoffen Mit Überkritischen Komprimierten Gasen Unter Verwendung Von Schleppmitteln. Ph.D. Thesis, Technische Universität Hamburg, Hamburg, Germany, 2000.
49. Galanakis, C.M. Recovery of high added-value components from food wastes: Conventional, emerging technologies and commercialized applications. *Trends Food Sci. Technol.* **2012**, *26*, 68–87, doi:10.1016/j.tifs.2012.03.003.
50. Golberg, A.; Sack, M.; Teissie, J.; Pataro, G.; Pliquet, U.; Saulis, G.; Stefan, T.; Miklavčič, D.; Vorobiev, E.; Frey, W. Energy-efficient biomass processing with pulsed electric fields for bioeconomy and sustainable development. *Biotechnol. Biofuels* **2016**, *9*, 94, doi:10.1186/s13068-016-0508-z.
51. Elez-Martinez, P.; Martín-Belloso, O. Effects of high intensity pulsed electric field processing conditions on vitamin C and antioxidant capacity of orange juice and gazpacho, a cold vegetable soup. *Food Chem.* **2007**, *102*, 201–209, doi:10.1016/j.foodchem.2006.04.048.

52. Gachovska, T.; Cassada, D.; Subbiah, J.; Hanna, M.; Thippareddi, H.; Snow, D. Enhanced Anthocyanin Extraction from Red Cabbage Using Pulsed Electric Field Processing. *J. Food Sci.* **2010**, *75*, E323–E329, doi:10.1111/j.1750-3841.2010.01699.x.
53. Luthria, D.L.; Biswas, R.; Natarajan, S.; Comparison of extraction solvents and techniques used for the assay of isoflavones from soybean. *Food Chem.* **2007**, *105*, 325–333, doi.org/10.1016/j.foodchem.2006.11.047.
54. Sheikh, J.; Jagtap, P.S.; Teli, M.D. Ultrasound assisted extraction of natural dyes and natural mordants vis a vis dyeing. *Fibers Polym.* **2016**, *17*, 738–743, doi:10.1007/s12221-016-5031-0.
55. Sivakumar, V.; Anna, J.L.; Vijayeeswarri, J.; Swaminathan, G. Ultrasound assisted enhancement in natural dye extraction from beetroot for industrial applications and natural dyeing of leather. *Ultrason. Sonochemistry* **2009**, *16*, 782–789, doi:10.1016/j.ultsonch.2009.03.009.
56. Saxena, S.; Raja, A.S.M. *Natural Dyes: Sources, Chemistry, Application and Sustainability Issues*; in Muthu S. (eds) Roadmap to Sustainable Textiles and Clothing. Textile Science and Clothing Technology, Springer: Singapore, **2014**; pp. 37–80.
57. Gala, S.; Sumarno, S.; Mahfud, M. Microwave-assisted Extraction of Natural Dyes from *Coleus atropurpureus* Leaves: The Effect of Solvent. *MATEC Web Conf.* **2018**, *156*, 06011, doi:10.1051/mateconf/201815606011.
58. Ain, J.N.; Sakinah, A.M.M.; Zularisam, A.W. Effects of different extraction conditions on the production of anthraquinone. *AJBAS* **2016**, *10*, 128–135.
59. Ramadevi, S.; Kalaiaresi, K. Optimization of microwave-assisted extraction of natural dye from *Ricinus communis* L leaves. *Int. J. Adv. Sci. Eng.* **2015**, *2*, 98–102.
60. Kamel, M.; El-Shishtawy, M.; Yussef, B.M.; Mashaly, H. Ultrasonic assisted dyeing: III. Dyeing of wool with lac as a natural dye. *Dye. Pigm.* **2005**, *65*, 103–110.
61. US EPA. 40CFR Part 50: Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient air (Appendix G); Federal Register 44; US Government Printing Office: Washington, DC, USA, 1979; p. 564.
62. Ashley, K. Ultrasonic extraction and field-portable anodic stripping voltammetry of lead from environmental samples. *Electroanal* **1995**, *7*, 1189–1192, doi:10.1002/elan.1140071217.
63. Porto, C.D.; Decorti, D.; Kikic, I. Flavour compounds of *Lavandula angustifolia* L. to use in food manufacturing: Comparison of three different extraction methods. *Food Chem.* **2009**, *112*, 1072–1078, doi:10.1016/j.foodchem.2008.07.015.
64. Chemat, S.; Lagha, A.; Aitamar, H.; Bartels, P.V.; Chemat, F. Comparison of conventional and ultrasound-assisted extraction of carvone and limonene from caraway seeds. *Flavour Fragr. J.* **2004**, *19*, 188–195, doi:10.1002/ffj.1339.
65. Asfaw, N.; Licence, P.; Novitskii, A.A.; Poliakoff, M. Green chemistry in Ethiopia: the cleaner extraction of essential oils from *Artemisia afra*: a comparison of clean technology with conventional methodology. *Green Chem.* **2005**, *7*, 352–356, doi.org/10.1039/B417961G.
66. Kimbaris, C.A.C.N.G.; Daferera, S.D.J.; Tarantilis, P.A.; Pappas, C.S.; Polissiou, M.G. Comparison of distillation and ultrasound-assisted extraction methods for the isolation of sensitive aroma compounds from garlic (*Allium sativum*). *Ultrason. Sonochem.* **2006**, *13*, 54–60.
67. Chemat, F.; Rombaut, N.; Sicaire, A.-G.; Meullemiestre, A.; Fabiano-Tixier, A.-S.; Vian, M.A. Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review. *Ultrason. Sonochem.* **2017**, *34*, 540–560, doi:10.1016/j.ultsonch.2016.06.035.
68. Alupului, A.; Călinescu, I.; Lavric, V. Microwave extraction of active principles from medicinal plants. *UPB Sci. Bull. Ser. B* **2012**, *74*, 129–142.
69. Sahena, F.; Zaidul, I.; Jinap, S.; Karim, A.; Abbas, K.; Norulaini, N.; Omar, A. Application of supercritical CO₂ in lipid extraction—A review. *J. Food Eng.* **2009**, *95*, 240–253, doi:10.1016/j.jfoodeng.2009.06.026.
70. Chen, X.; Zhag, M.; Xu, B.; Adhikari, B.; Sun, J. The principles of ultrasound and its application in freezing related processes in the food industry: a review. *Ultrason. Sonochem.* **2015**, *21*, 576–585.
71. Orphanides, A.; Goulas, V.; Gekas, V. Introducing the concept of sono-chemical potential: a phenomenological model for ultrasound assisted extraction. *J. Food Eng.* **2014**, *120*, 191–196.
72. Bosisio, R.G.; Cambon, J.L.; Chavarie, C.; Klvana, D. Experimental results on the heating of Athabasca tar sand samples with microwave power. *J. Microw. Power* **1977**, *12*, 301–307.
73. Balint, V.; Pinter, A.; Mika, G. Process for the Recovery of Shale Oil, Heavy Oil, Kerogen, or Tar from Their Natural Sources. Patent US 4419214, 6 December 1981.

74. Tong, L.; Liu, H.; Xie, C.; Li, M. Quantitative analysis of antibiotics in aquifer sediments by liquid chromatography coupled to high resolution mass spectrometry. *J. Chromatogr. A* **2016**, *1452*, 58–66, doi:10.1016/j.chroma.2016.05.027.
75. Mohapatra, D.; Brar, S.K.; Tyagi, R.; Picard, P.; Surampalli, R. Carbamazepine in municipal wastewater and wastewater sludge: Ultrafast quantification by laser diode thermal desorption-atmospheric pressure chemical ionization coupled with tandem mass spectrometry. *Talanta* **2012**, *99*, 247–255, doi:10.1016/j.talanta.2012.05.047.
76. Li, Y.; Fabiano-Tixier, A.S.; Vian, M.A.; Chemat, F. Solvent-free microwave extraction of bioactive compounds provides a tool for green analytical chemistry. *TrAC Trends Anal. Chem.* **2013**, *47*, 1–11, doi:10.1016/j.trac.2013.02.007.
77. Montesdeoca-Esponda, S.; Sosa-Ferrera, Z.; Santana-Rodriguez, J.J. Combination of microwave-assisted micellar extraction with liquid chromatography tandem mass spectrometry for the determination of fluoroquinolone antibiotics in coastal marine sediments and sewage sludges samples. *Biomed. Chromatogr.* **2012**, *26*, 33–40.
78. Dorival-Garcia, N.; Zafra-Gomez, A.; Camino-Sanchez, F.J.; Navalon, A.; Vilchez, J.L. Analysis of quinolone antibiotic derivatives in sewage sludge samples by liquid chromatography-tandem mass spectrometry: comparison of the efficiency of three extraction techniques. *Talanta* **2013**, *106*, 104–118.
79. Speltini, A.; Sturini, M.; Maraschi, F.; Viti, S.; Sbarbada, D.; Profumo, A. Fluoroquinolone residues in compost by green enhanced microwave-assisted extraction followed by ultra performance liquid chromatography tandem mass spectrometry. *J. Chromatogr. A* **2015**, *1410*, 44–50.
80. Koh, P.C.; Leong, C.M.; Noranizan, M.A. Microwave-assisted extraction of pectin from jackfruit rinds using different power levels. *Int. Food Res. J.* **2014**, *21*, 2091–2097.
81. Rafiee, Z.; Jafari, S.M.; Alami, M.; Khomeiri, M. Microwave-assisted extraction of phenolic compounds from olive leaves-A comparison with maceration. *J. Anim. Plant Sci.* **2011**, *21*, 738–745.
82. İnce, A.E.; Şahin, S.; Şümnü, S.G. Extraction of phenolic compounds from melissa using microwave and ultrasound. *Turk J. Agric. For.* **2013**, *37*, 69–75.
83. Sinha, K.; Das Saha, P.; Datta S. Response surface optimization and artificial neural network modeling of microwave assisted natural dye extraction from pomegranate rind. *Ind. Crop. Prod.* **2012**, *37*, 408–414, doi.org/10.1016/j.indcrop.2011.12.032.
84. Raza, A.; Iqbal, N.; Mahmood, S.; Parveen, S.; Azeem, M.; Nawaz, M.; Javed, M.; Noman, A. Harnessing Natural Colorants for Sustainable Textile Dyeing an Eco-Friendly Approach Using Sweet Cane (*Saccharum Bengalense* Retz.) Inflorescence. *Braz. Arch. Boil. Technol.* **2018**, *61*, doi:10.1590/1678-4324-2018170802.
85. Yoshida, T.; Tsubaki, S.; Teramoto, Y.; Azuma, J.-I. Optimization of microwave-assisted extraction of carbohydrates from industrial waste of corn starch production using response surface methodology. *Bioresour. Technol.* **2010**, *101*, 7820–7826, doi:10.1016/j.biortech.2010.05.011.
86. Petersson, E.V.; Liu, J.; Sjöberg, P.J.; Danielsson, R.; Turner, C. Pressurized hot water extraction of anthocyanins from red onion: A study on extraction and degradation rates. *Anal. Chim. Acta.* **2010**, *663*, 27–32, doi.org/10.1016/j.aca.2010.01.023.
87. Blasco, C.; Di Corcia, A.; Picó, Y. Determination of tetracyclines in multi-specie animal tissues by pressurized liquid extraction and liquid chromatography–tandem mass spectrometry. *Food Chem.* **2009**, *116*, 1005–1012, doi:10.1016/j.foodchem.2009.03.055.
88. McClure, E.L.; Wong, C. Solid phase microextraction of macrolide, trimethoprim, and sulfonamide antibiotics in wastewaters. *J. Chromatogr. A* **2007**, *1169*, 53–62, doi:10.1016/j.chroma.2007.08.062.
89. Kwang, H.C.; Hee, J.L.; Song, Y.K.; Dae-Geun, S.; Dong-Un, L.; Cheol-Ho, P. Optimization of Pressurized Liquid Extraction of Carotenoids and Chlorophylls from *Chlorella vulgaris*. *J. Agric. Food Chem.* **2010**, *58*, 793–797.
90. Lin, S.-C.; Chang, C.-M.J.; Deng, T.-S. Enzymatic hot pressurized fluids extraction of polyphenolics from *Pinus taiwanensis* and *Pinus morrissonicola*, *J. Taiwan Inst. Chem. Engrs.* **2009**, *40*, 136–142.
91. Deng, C.H.; Li, N.; Zhang, X.M. Rapid determination of essential oil in *Acorus tatarinowii* Schott by pressurized hot water extraction followed by solidphase microextraction and gas chromatography-mass spectrometry. *J. Chromatogr. A* **2004**, *1059*, 149–155.
92. Deng, C.H.; Yao, N.; Wang, A.Q.; Zhang, X.M. Determination of essential oil in a traditional Chinese medicine *Fructus amomi* by pressurized hot water extraction followed by liquid-phase microextraction and gas chromatography-mass spectrometry. *Anal. Chim. Acta.* **2005**, *536*, 237–244.

93. Eller, F.J.; Taylor, S.L. Pressurized fluids for extraction of cedarwood oil from *juniperus virginiana*. *J. Agril. Food Chem.* **2004**, *52*, 2335–2338.
94. Parniakov, O.; Lebovka, N.I.; Van Hecke, E.; Vorobiev, E.; Nikolai, L. Pulsed Electric Field Assisted Pressure Extraction and Solvent Extraction from Mushroom (*Agaricus bisporus*). *Food Bioprocess Technol.* **2013**, *7*, 174–183, doi:10.1007/s11947-013-1059-y.
95. Putnik, P.; Lorenzo, J.; Barba, F.; Roohinejad, S.; Jambrak, A.R.; Granato, D.; Montesano, D.; Kovačević, D.B. Novel Food Processing and Extraction Technologies of High-Added Value Compounds from Plant Materials. *Foods* **2018**, *7*, 106, doi:10.3390/foods7070106.
96. Syed, Q.A.; Syed, A.I.Q.A.; Rahman, S.A.U.U. Pulsed Electric Field Technology in Food Preservation: A Review. *J. Nutr. Heal. Food Eng.* **2017**, *6*, 1–5, doi:10.15406/jnhfe.2017.06.00219.
97. Parniakov, O.; Barba, F.; Grimi, N.; Marchal, L.; Jubeau, S.; Lebovka, N.; Vorobiev, E. Pulsed electric field and pH assisted selective extraction of intracellular components from microalgae *Nannochloropsis*. *Algal. Res.* **2015**, *8*, 128–134, doi:10.1016/j.algal.2015.01.014.
98. Dawidowicz, A.L.; Rado, E.; Wianowska, D.; Mardarowicz, M.; Gawdzik, J. Application of PLE for the determination of essential oil components from *Thymus vulgaris* L. *Talanta* **2008**, *76*, 878–884, doi:10.1016/j.talanta.2008.04.050.
99. Moubarik, A.; El-Belghiti, K.; Vorobiev, E. Kinetic model of solute aqueous extraction from Fennel (*Foeniculum vulgare*) treated by pulsed electric field, electrical discharges and ultrasonic irradiations. *Food Bioprod. Process.* **2011**, *89*, 356–361, doi:10.1016/j.fbp.2010.09.002.
100. Segovia, F. J.; Luengo, E.; Corral-Pérez, J. J.; Raso, J.; Almajano, M. P. Improvements in the aqueous extraction of polyphenols from borage (*Borago officinalis* L.) leaves by pulsed electric fields: Pulsed electric fields (PEF) applications. *Industrial. Crop. Prod.* **2015**, *65*, 390–396.
101. Jäger, H.; Schulz, M.; Lu, P.; Knorr, D. Adjustment of milling, mash electroporation and pressing for the development of a PEF assisted juice production in industrial scale. *Innov. Food Sci. Emerg. Technol.* **2012**, *14*, 46–60, doi:10.1016/j.ifset.2011.11.008.
102. Sakaki, K.; Yokochi, T.; Suzuki, O.; Hakuta, T. Supercritical fluid extraction of fungal oil using CO₂, N₂O, CHF₃ and SF₆. *J. Am. Oil Chem. Soc.* **1990**, *67*, 553–557, doi:10.1007/bf02540765.
103. Capuzzo, A.; Maffei, M.E.; Occhipinti, A. Supercritical Fluid Extraction of Plant Flavors and Fragrances. *Molecules* **2013**, *18*, 7194–7238, doi:10.3390/molecules18067194.
104. Zhang, Y.; Zhang, X.; Chi, S.; Li, Z. Pulping of bamboo using supercritical ammonia with recovery and reuse of the ammonia. *BioRes* **2019**, *14*, 5586–5594.
105. Gandhi, K.; Arora, S.; Kumar, A. Industrial applications of supercritical fluid extraction: A review. *Int. J. Chem. Stud.* **2017**, *5*, 336–340.
106. Herrero, M.; Cifuentes, A.; Ibanez, E. Sub- and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae A review. *Food Chem.* **2006**, *98*, 136–148, doi:10.1016/j.foodchem.2005.05.058.
107. Romo-Hualde, A.; Yetano-Cunchillos, A.I.; González-Ferrero, C.; Sáiz-Abajo, M.J.; González-Navarro, C.J. Supercritical fluid extraction and microencapsulation of bioactive compounds from red pepper (*Capsicum annum* L.) by-products. *Food Chem.* **2012**, *133*, 1045–1049, doi.org/10.1016/j.foodchem.2012.01.062.
108. Nautiyal, O.H. Food processing by supercritical carbon dioxide-review. *EC Chem.* **2016**, *2*, 111–135.
109. Brunner, G. Supercritical fluids: technology and application to food processing. *J. Food Eng.* **2005**, *67*, 21–33.
110. Guedes, A.C.; Gião, M.S.; Matias, A.A.; V.M.Nunes, A.; Pintado, M.E.; Duarte, C.; Malcata, F.X.; Pintado, M.M. Supercritical fluid extraction of carotenoids and chlorophylls a, b and c, from a wild strain of *Scenedesmus obliquus* for use in food processing. *J. Food Eng.* **2013**, *116*, 478–482, doi:10.1016/j.jfoodeng.2012.12.015.
111. Saus, W.; Knittel, D.; Schollmeyer, E. Dyeing of Textiles in Supercritical Carbon Dioxide. *Text. Res. J.* **1993**, *63*, 135–142, doi:10.1177/004051759306300302.
112. Sanchez-Sanchez, J.; Ponce, M.T.F.; Casas, L.; Mantell, C.; De La Ossa, E.M. Impregnation of mango leaf extract into a polyester textile using supercritical carbon dioxide. *J. Supercrit. Fluids* **2017**, *128*, 208–217, doi:10.1016/j.supflu.2017.05.033.
113. Munshi, P.; Bhaduri, S. Supercritical CO₂: A twenty-first century solvent for the chemical industry. *Curr. Sci. India* **2009**, *97*, 63–72.
114. Wang, S.; Kienzle, F. The synthesis of pharmaceutical intermediates in supercritical fluids. *Ind. Eng. Chem. Res.* **2000**, *39*, 4487–4490.

115. Hyde, J.R.; Poliakov, M. Supercritical hydrogenation and acid-catalysed reactions without gases? *Chem. Commun.* **2004**, *13*, 1482–1483, doi:10.1039/b404181j.
116. Cardarelli, C.R.; Benassi, M.D.T.; Mercadante, A.Z. Characterization of different annatto extracts based on antioxidant and colour properties. *LWT* **2008**, *41*, 1689–1693, doi:10.1016/j.lwt.2007.10.013.
117. Jiao, Z.; Guo, Z.; Zhang, S.; Chen, H. Microwave-assisted micro-solid-phase extraction for analysis of tetracycline antibiotics in environmental samples. *Int. J. Environ. Anal. Chem.* **2014**, *95*, 82–91, doi:10.1080/03067319.2014.983497.
118. Samedova, F.I.; Gasanova, R.Z.; Kasumova, A.M.; Rashidova, S.Y.; Kuliye, A.D.; Aliyev, B.M.; Kafarova, N.F. Summary of the Monograph of F. I. Samedova “The Application of Supercritical Fluids in Petroleum and Oil Fractions Refining.” *Voice Publ.* **2015**, *1*, 17–25, doi:10.4236/vp.2015.11003.
119. Xiao, J.; Chen, G.; Li, N. Ionic Liquid Solutions as a Green Tool for the Extraction and Isolation of Natural Products. *Molecules* **2018**, *23*, 1765, doi:10.3390/molecules23071765.
120. Ventura, S.P.M.; Silva, F.; Quental, M.J.; Mondal, D.; Freire, M.G.; Coutinho, J.A.P. Ionic-Liquid-Mediated Extraction and Separation Processes for Bioactive Compounds: Past, Present, and Future Trends. *Chem. Rev.* **2017**, *117*, 6984–7052, doi:10.1021/acs.chemrev.6b00550.
121. Seddon, K.R. Ionic Liquids for Clean Technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356, doi:10.1002/(sici)1097-4660(199704)68:43.0.co;2-4.
122. Welton, T. Ionic liquids: a brief history. *Biophys. Rev.* **2018**, *10*, 691–706, doi:10.1007/s12551-018-0419-2.
123. Anastas, P.T.; Wasserscheid, P.; Stark, A. *Handbook of Green Chemistry, Volume 6, Green Solvents, Ionic Liquids*; Wiley-VCH: Weinheim, Germany, 2013.
124. Iacob, C.; Sangoro, J.R.; Kipnusu, W.K.; Valiullin, R.; Kärger, J.; Kremer, F. Enhanced charge transport in nano-confined ionic liquids. *Soft Matter* **2012**, *8*, 289–293, doi:10.1039/c1sm06581e.
125. Santos, L.M.N.B.F.; Canongia Lopes, J.N.; Coutinho, J.A.P.; Esperança, J.M.S.S.; Gomes, L.R.; Marrucho, I.M.; Rebelo, L.P.N. Ionic liquids: first direct determination of their cohesive energy. *J. Am. Chem. Soc.* **2006**, *129*, 284–285.
126. Haddleton, D.M.; Welton, T.; Carmichael, A.J. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2008; pp. 619–640.
127. Endres, F.; El Abedin, S.Z. Air and water stable ionic liquids in physical chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101, doi:10.1039/b600519p.
128. Rooney, D.W.; Jacquemin, J.; Gardas, R.L. Thermophysical Properties of Ionic Liquids. *Chemical Diagnostics* **2009**, *290*, 185–212, doi:10.1007/128_2008_32.
129. Tang, B.; Bi, W.; Tian, M.; Row, K.H. Application of ionic liquid for extraction and separation of bioactive compounds from plants. *J. Chromatogr. B* **2012**, *904*, 1–21, doi:10.1016/j.jchromb.2012.07.020.
130. Pu, Y.; Jiang, N.; Ragauskas, A. Ionic Liquid as a Green Solvent for Lignin. *J. Wood Chem. Technol.* **2007**, *27*, 23–33, doi:10.1080/02773810701282330.
131. Zhao, H.; Xia, S.; Ma, P. Use of ionic liquids as ‘green’ solvents for extractions. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1089–1096, doi:10.1002/jctb.1333.
132. Mekki, S.; Wai, C.M.; Billard, I.; Moutiers, G.; Burt, J.; Yoon, B.; Wang, J.S.; Gaillard, C.; Ouadi, A.; Hesemann, P. Extraction of Lanthanides from Aqueous Solution by Using Room-Temperature Ionic Liquid and Supercritical Carbon Dioxide in Conjunction. *Chem.-A Eur. J.* **2006**, *12*, 1760–1766, doi:10.1002/chem.200500559.
133. Wang, J.S.; Sheaff, C.N.; Yoon, B.; Addleman, R.S.; Wai, C.M. Extraction of Uranium from Aqueous Solutions by Using Ionic Liquid and Supercritical Carbon Dioxide in Conjunction. *Chem.-A Eur. J.* **2009**, *15*, 4458–4463, doi:10.1002/chem.200801415.
134. Freitas, A.C.D.; Cunico, L.P.; Aznar, M.; Guirardello, R. Modeling vapor liquid equilibrium of ionic liquids + gas binary systems at high pressure with cubic equations of state. *Braz. J. Chem. Eng.* **2013**, *30*, 63–73, doi:10.1590/s0104-66322013000100008.
135. Keskin, S.; Kayrak-Talay, D.; Akman, U.; Hortacsu, O. A review of ionic liquids towards supercritical fluid applications. *J. Supercrit. Fluid* **2007**, *43*, 150–180.
136. Blanchard, L.A.; Brennecke, J.F. Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292, doi:10.1021/ie000710d.
137. Kroon, M.C.; Van Spronsen, J.; Peters, C.J.; Sheldon, R.A.; Witkamp, G.-J. Recovery of pure products from ionic liquids using supercritical carbon dioxide as a co-solvent in extractions or as an anti-solvent in precipitations. *Green Chem.* **2006**, *8*, 246–249, doi:10.1039/b512303h.

138. Zaitsau, D.H.; Paulechka, Y.U.; Kabo, G.J. The Kinetics of Thermal Decomposition of 1-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. A* **2006**, *110*, 11602–11604, doi:10.1021/jp064212f.
139. Blanchard, L.A.; Gu, Z.; Brennecke, J.F. High-Pressure Phase Behavior of Ionic Liquid/CO₂ Systems. *J. Phys. Chem. B* **2001**, *105*, 2437–2444, doi:10.1021/jp003309d.
140. Tomida, D.; Kumagai, A.; Kenmochi, S.; Qiao, K.; Yokoyama, C. Viscosity of 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Octyl-3-methylimidazolium Hexafluorophosphate at High Pressure. *J. Chem. Eng. Data* **2007**, *52*, 577–579, doi:10.1021/je060464y.
141. De Azevedo, R.G.; Esperança, J.M.S.S.; Najdanovic-Visak, V.; Visak, Z.; Guedes, H.J.R.; Da Ponte, M.N.; Rebelo, L.P.N. Thermophysical and Thermodynamic Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate over an Extended Pressure Range. *J. Chem. Eng. Data* **2005**, *50*, 997–1008, doi:10.1021/je049534w.
142. Jaganathan, J.R.; Sivapragasam, M.; Wilfred, C.D. Thermal Characteristics of 1-Butyl-3-Methylimidazolium Based Oxidant Ionic Liquids. *J. Biosens. Bioelectron.* **2016**, *7*, 309, doi:10.4172/2157-7048.1000309.
143. Zhou, Q.; Wang, L.-S.; Chen, H.-P. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H₂O Binary Mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905–908, doi:10.1021/je050387r.
144. Babucci, M.; Akçay, A.; Balci, V.; Uzun, A. Thermal Stability Limits of Imidazolium Ionic Liquids Immobilized on Metal-Oxides. *Langmuir* **2015**, *31*, 9163–9176, doi:10.1021/acs.langmuir.5b02519.
145. Bogdanov, M.; Kantlehner, W. Simple Prediction of Some Physical Properties of Ionic Liquids: The Residual Volume Approach. *Z. Nat. B* **2009**, *64*, 215–222, doi:10.1515/znb-2009-0212.
146. Mokhtarani, B.; Sharifi, A.; Mortaheb, H.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and viscosity of 1-butyl-3-methylimidazolium nitrate with ethanol, 1-propanol, or 1-butanol at several temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 1432–1438, doi:10.1016/j.jct.2009.06.023.
147. Schmidt, H.; Stephan, M.; Safarov, J.; Kul, I.; Nocke, J.; Abdulagatov, I.; Hassel, E. Experimental study of the density and viscosity of 1-ethyl-3-methylimidazolium ethyl sulfate. *J. Chem. Thermodyn.* **2012**, *47*, 68–75, doi:10.1016/j.jct.2011.09.027.
148. Cao, Y.; Mu, T. Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 8651–8664, doi:10.1021/ie5009597.
149. Reddy, R.G.; Zhang, Z.; Arenas, M.F.; Blake, D.M. Thermal Stability and Corrosivity Evaluations of Ionic Liquids as Thermal Energy Storage Media. *High Temp. Mater. Process.* **2003**, *22*, 87–94, doi:10.1515/htmp.2003.22.2.87.
150. Mokhtarani, B.; Sharifi, A.; Mortaheb, H.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and viscosity of pyridinium-based ionic liquids and their binary mixtures with water at several temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 323–329, doi:10.1016/j.jct.2008.09.001.

