Ultrasonics Sonochemistry 34 (2017) 540–560

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Review

Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review

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ARTICLE INFO

Article history:
Received 4 April 2016
Received in revised form 9 June 2016
Accepted 23 June 2016
Available online 23 June 2016

Keywords:
Ultrasound-assisted extraction
Mechanisms
Hybrid techniques
Safety and security
Green impacts
Industrial application

ABSTRACT

This review presents a complete picture of current knowledge on ultrasound-assisted extraction (UAE) in food ingredients and products, nutraceutics, cosmetic, pharmaceutical and bioenergy applications. It provides the necessary theoretical background and some details about extraction by ultrasound, the techniques and their combinations, the mechanisms (fragmentation, erosion, capillarity, detexturation, and sonoporation), applications from laboratory to industry, security, and environmental impacts. In addition, the ultrasound extraction procedures and the important parameters influencing its performance are also included, together with the advantages and the drawbacks of each UAE techniques. Ultrasound-assisted extraction is a research topic, which affects several fields of modern plant-based chemistry. All the reported applications have shown that ultrasound-assisted extraction is a green and economically viable alternative to conventional techniques for food and natural products. The main benefits are decrease of extraction and processing time, the amount of energy and solvents used, unit operations, and CO_2 emissions.

Contents

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http://dx.doi.org/10.1016/j.ultsonch.2016.06.035
1350-4177/

1. Introduction

Extraction has been used probably since the discovery of fire. Egyptians and Phoenicians, Jews and Arabs, Indians and Chinese, Greeks and Romans, and even Mayas and Aztecs, all possessed innovative extraction and distillation processes used even for perfumes, cosmetics or food. Nowadays, we cannot find a production line in food, pharmaceutical, cosmetic, nutraceutic, or bioenergy industries, which do not use extraction processes, such as (maceration, solvent extraction, steam or hydro-distillation, cold pressing, squeezing...). With the increasing energy costs and the drive to reduce greenhouse gas emissions, food and plant-based chemical industries are challenged to find new technologies in order to reduce energy consumption, to meet legal requirements on emissions, product/process safety and control, and for cost reduction and increased quality as well as functionality. For example, existing extraction technologies have considerable technological and scientific bottlenecks to overcome: often requiring up to 50% of investments in a new plant and more than 70% of total process energy used in food industries [1]. In the last two decades, these shortcomings have led to the consideration of the use of enhanced and efficient extraction techniques amenable to automation such as ultrasound-assisted extraction. Shorter extraction times, reduced organic solvent consumption, energy and costs saved, were the main tasks pursued. Driven by these goals, advances in ultrasound-assisted extraction have resulted in a number of innovative techniques such as ultrasound-assisted Soxhlet extraction, ultrasound-assisted Clevenger distillation, continuous ultrasound-assisted extraction, and combination of ultrasound with other techniques such as microwave, extrusion, and supercritical fluid extraction.

To meet the requirements of the market and of the regulations, the sono-extract must meet a number of quality criteria, contrary to some popular misconceptions; the "natural" state of the extract is no guarantee of its harmlessness to human and its environment. In such changing context, nowadays we must include the change of extraction conscience from a simple interest in data analysis to interest in models and the strong consideration of the environmental side effects of our practice as a consequence of the high demand of extraction information. This evolution or revolution of extraction of natural products is resumed in Fig. 1. Green extraction of naturals products could be a new concept to meet the challenges of the 21st century, to protect both the environment and consumers and in the meantime enhance competition of industries to be more ecologic, economic and innovative [2,3].

Ultrasound is a key-technology in achieving the objective of sustainable "green" chemistry and extraction. Ultrasound is well known to have a significant effect on the rate of various processes in the chemical and food industry. Using ultrasound, full extractions can now be completed in minutes with high reproducibility, reducing the consumption of solvent, simplifying manipulation and work-up, giving higher purity of the final product, eliminating post-treatment of waste water and consuming only a fraction of the fossil energy normally needed for a conventional extraction method such as Soxhlet extraction, maceration or Clevenger distillation. Several classes of food components such as aromas, pigments, antioxidants, and other organic and mineral compounds have been extracted, analyzed and formulated efficiently from a variety of matrices (mainly animal tissues, microalgae, yeasts, food and plant materials).

This review presents a complete picture of current knowledge on ultrasound-assisted extraction of food and natural products. The readers like chemists, biochemists, chemical engineers, physicians, and food technologists even from academia or industry will find a deep and complete perspective regarding ultrasound-assisted extraction. This review will not systematically address the following topics, which were pertinently covered by recent reviews:

- Ultrasound cavitation theory [4];
- Guidelines of good practice for UAE [5];
- Application of ultrasound in food processing [6].

The first part presents the different mechanisms involved during UAE (fragmentation, erosion, capillarity, detexturation, and sonoporation) and influencing parameters. The second part is dedicated to the importance of the ultrasound techniques and their combinations. The third part focuses on applications of UAE in different fields and presentation of most relevant procedures. The last part gives new insights in term of up-scaling and industrial applications, quality, security and safety considerations, environmental impacts and future directions for research and industry.

2. Extraction mechanisms induced by ultrasound

UAE of natural products has been widely investigated, with numerous examples, which could be found in literature. Additionally, a few very good reviews on the subject were published within the last years [6–9]. However in these reviews and throughout

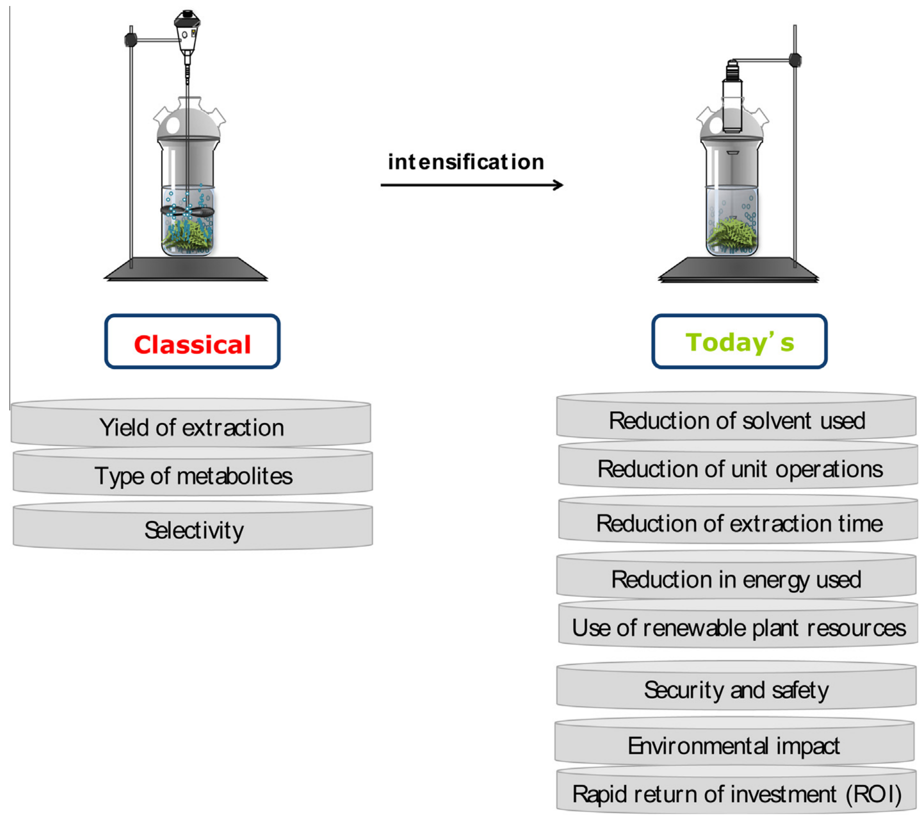

Fig. 1. Ultrasound-assisted extraction: evolution or revolution.

literature, mechanisms leading to extraction enhancement due to the use of ultrasound are rarely investigated. Some reference papers describe the effects of ultrasound propagation in a solid/liquid media [10,11]. Cavitation phenomena leads to high shear forces in the media. The implosion of cavitation bubbles on a product's surface results in micro-jetting which generates several effects such as surface peeling, erosion and particle breakdown. Additionally, implosion of cavitation bubbles in a liquid media leads to macro-turbulences and to a micro mixing. Surprisingly, in most publications dealing with UAE of natural products, the authors justify yields enhancement by cavitation effects occurring during ultrasonic irradiation without further investigations.

Toma et al. (2001) [12] demonstrated that a fragmentation of the matrix occurred during irradiation and an enhanced hydration of the matrix due to ultrasound. The authors also showed an increase of the extraction index for sonicated samples compared to non-sonicated samples. To pursue the understanding and illustrate the ultrasound effect on a vegetal matrix during UAE, we examined closely different studies and we noticed that ultrasound extraction doesn't act with one mechanism but through different independent or combined mechanisms between fragmentation, erosion, capillarity, detexturation, and sonoporation. The following section aims at highlighting physical impacts of ultrasound on a vegetal matrix, which could be linked to extraction yield increase. All studies refer to high power ultrasound corresponding to frequencies of 20 or 25 kHz.

2.1. Fragmentation

In some cases, during application of ultrasound in a liquid media containing a raw material, it can be noticed a rapid fragmentation of the raw material. The impact of fragmentation induced by ultrasound is illustrated in this section throughout the example of chlorophyll extraction from spinach leaves (Fig. 2). This effect was examined using an ultrasound probe (20 kHz, UIP1000 HdT, Hielscher). During UAE, it was noticed a quick fragmentation of the spinach leaves in the first minutes of sonication whereas leaves did not seems impacted during conventional extraction performed by maceration. The extraction kinetics of chlorophylls from spinach has been monitored by UV (Fig. 2-A). Comparing the extraction rate of chlorophylls between UAE process and maceration process, a linear increase is obtained at the beginning of UAE, corresponding to a direct solubilization of chlorophylls. This effect is most probably due to the reduction in particle size occurring during application of ultrasound. Spinach residues were collected after filtration to measure the particle size distribution (Fig. 2-B). On the chart are plotted particle size distributions below 1100 μm for residues from UAE and maceration. It has been noted that 80% of the sample mass for maceration particles are beyond 1100 μm and could not be measured by the same equipment. The average particle size of spinach residue after UAE (200 μm) is lower than the maceration one (300 μm). Fragmentation of friable solids resulting from ultrasonic cavitation has been identified by several authors [11,13,14]. Fragmentation can be due to inter-particle collisions and from shockwaves created from collapsing cavitation bubbles in the liquid. A direct consequence of the reduction in particle size by ultrasound action is the increase of surface area of the solid resulting in higher mass transfer and increased extraction rate and yield.

2.2. Erosion

Some authors have already noticed erosion of raw plant material when treated by ultrasound. For example, UAE of boldo leaves has been studied by Petigny et al. (2013) [15] using an ultrasonic probe (20 kHz, UIP1000 hd, Hielscher). Comparison of extraction

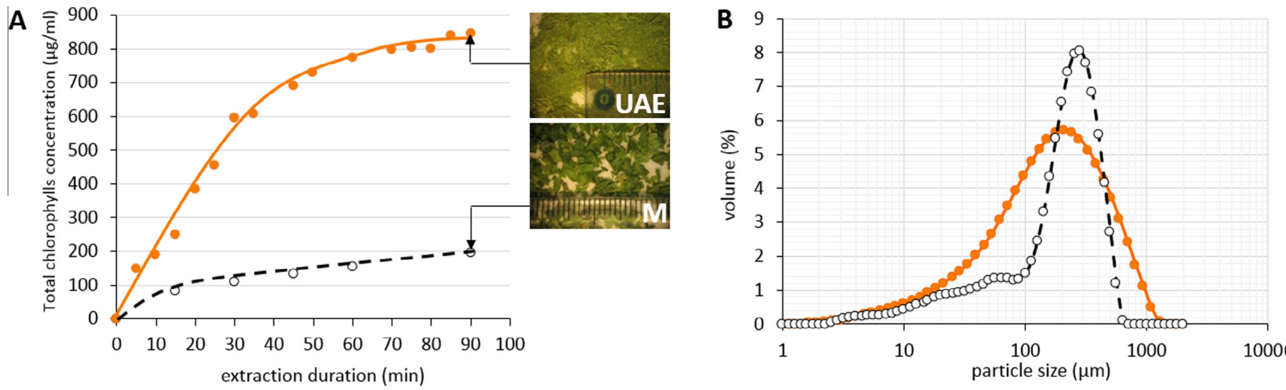

Fig. 2. Effect of power ultrasound on spinach leaves. (**A**: Comparison of chlorophyll extraction kinetics for UAE, US probe 20 kHz (●) and for maceration (M, ○); **B**: Comparison of particle size repartition (below 1 mm) of spinach residue for UAE (●) and for maceration (○)).

yields shows enhancement of extraction yield from 20% for conventional maceration to 25% with UAE (Fig. 3-A). Extraction rate enhancement is also noted during the first stage of extraction. Comparison of SEM observations of leaf surface before and after treatment show that leaves are not fragmented, but a localized effect has been noticed. Boldo leaves possess trichomes on the surface of leaves, which seems to be specifically impacted by ultrasound (Fig. 3-B). Hence, theses structure seem to have been damaged or removed from the leaf after ultrasound treatment, which is not the case of leaves submitted to maceration. The erosion enhanced accessibility of water as solvent to the leaf further improving extraction and solubilization. Given those observations,

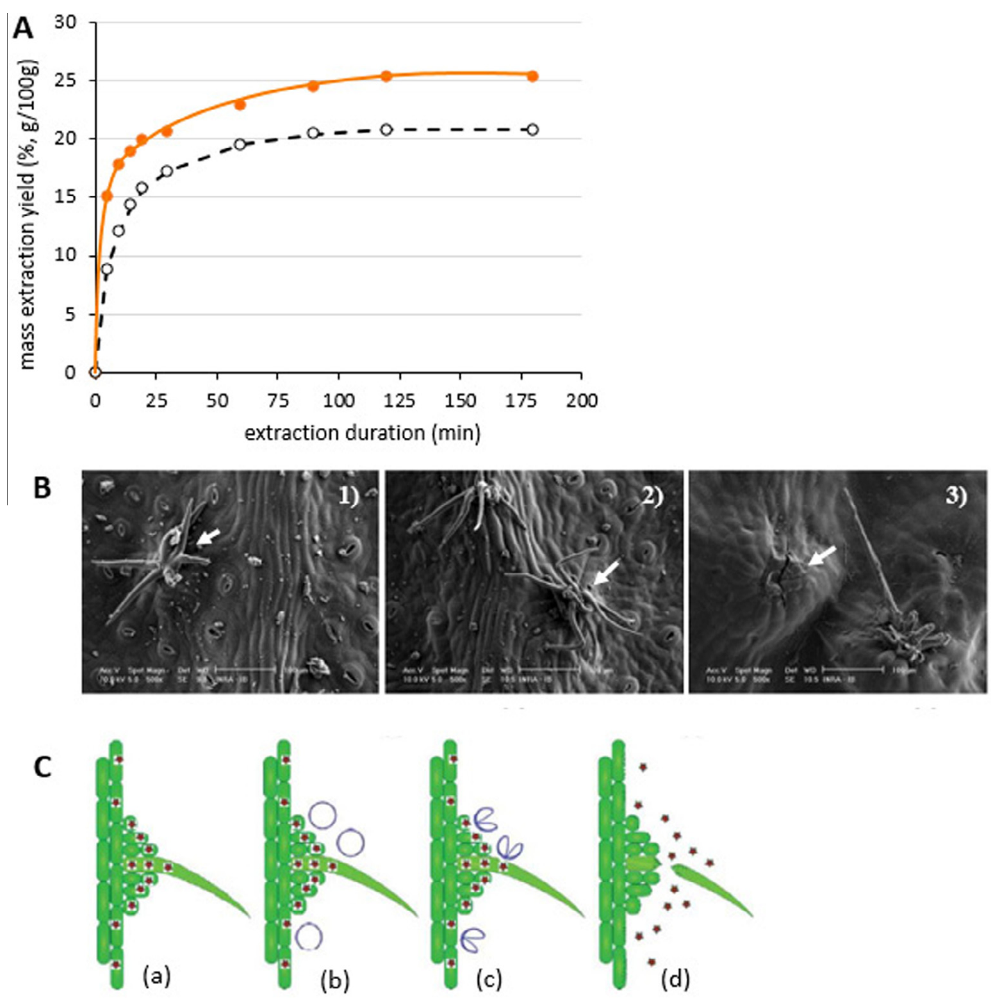

Fig. 3. Effect of power ultrasound on boldo leaves. (**A**: Comparison of extraction kinetics of soluble matter in water for UAE, US probe 20 kHz (●) and for maceration (○); **B**: SEM microscopic observation of trichomes on leaf surface, 1) control leaf surface, 2) leaf surface after conventional process, 3) leaf surface after UAE; **C**: Proposed mechanism for effect of cavitation bubbles on boldo leaf surface (**a**) Plant profile with a trichome at the surface of the leaf, (**b**) Generation of a cavitation bubble, (**c**) Collapse of the cavitation bubble which generates a micro-jet directed towards the surface and (**d**) Abrasion of the surface, breaking of the trichome, and release of soluble material in the surrounding medium).

a possible mechanism for extraction enhancement could be that implosion of cavitation bubbles on the leaves surface induces erosion of plant structures released in the extraction medium (Fig. 3-C). Erosion is a known effect of ultrasound and is used for several purposes such as cleaning or for sonochemical reactions e.g. with metals [16]. The study of Degrois et al., 1974 [17] had already identified an erosion on starch granules produced by acoustic cavitation. Numerous pits are visible on the surface of granules resulting from cavitation bubbles collapse.

2.3. Sonocapillary effect

The ultrasonic capillary effect (UCE) refers to the increase of depth and velocity of penetration of liquid into canals and pores under some conditions of sonication [18,19]. This effect induced by ultrasound has recently been experimentally demonstrated for molten aluminum by Tzanakis *et al.*, 2015 [20]. Although the mechanism for UCE is not fully understood, a relationship between cavitation and UCE has been established [21]. UCE could also be a mechanism explaining enhanced extraction performed under ultrasound.

In the study by Pingret et al., 2012 [22], recovery of total polyphenols from apple pomace was performed by ultrasound (Fig. 4-A). It can be identified that the extraction kinetics is improved under ultrasound, although the major difference in the two extraction processes seems to be occurring in the first 10 min of extraction. We hypothesized that the difference could be due to a water absorption further favoring solvent access and diffusion of polyphenol out of the pomace. For this, we performed an additional experiment by measuring the Water Holding Capacity (WHC) by a method described by Huang *et al.*, 2016 [23] (Fig. 4-B). The method was adapted to only 10 min to assess the effect of solid/liquid mixing (maceration by agitation and US). WHC is around 70% higher for ultrasound-treated pomace compared to maceration (Fig. 4-B). This observation confirms that water absorption is higher at the beginning of extraction and could contribute to explain the increase extraction yield during the first part of extraction.

The impact of UCE on extraction was proposed by Vinatoru (2001) [24]. The author also identified that the swelling index of several vegetable matrix was increased from 5 to 10% by using ultrasound and correlated this result to an increase of the extractive value of the tested vegetables matrices. By increasing the swelling and rehydration of a vegetable tissue, ultrasound impacts positively on the basic mechanisms of extractions: desorption and diffusion of a solute out of a vegetable structure. In this way, UCE directly acts on mass transfer improvement. The improvement of matrix WHC under ultrasound applied during meat brining or meat curing has also been investigated by several authors [25–29]. Authors reported a modification of meat structure after an ultrasound treatment as well as enhancement of salt and moisture transfer using ultrasound processing. The parameter which is reported to have a key influence is ultrasonic intensity, where a threshold value for ultrasound influence could be identified (e.g. between 40 and 50 W/cm^2 for pork loins ultrasound assisted brining [27]).

2.4. Sonoporation

The sonoporation effect of ultrasound is well-known in the field of biology and is applied when a permeability of cell membranes is desired. Sonoporation has been used *in vitro* for cell uptake in molecules e.g. drugs, genes (reversible sonoporation) or for cell destruction (irreversible sonoporation). For this, high ultrasound frequencies are applied (beyond 500 kHz) [30,31]. However, a few studies focus on the use of low frequency (20 kHz) for cell wall permeabilization [32] or bacteria inactivation [33].

In the field of extraction, sonoporation can be used for reversible or irreversible cell membrane pores, which would result in release of cellular content in the extractive medium. Work performed by our team on processing of wet yeast (*Yarrowia Lipolytca*) for recovery of oil in yeast cells, has been studied by ultrasound at 20 kHz [34]. In Fig. 5, a comparison is made between untreated yeast (Fig. 5-A) and US-treated yeast (Fig. 5-B). Yeasts treated by ultrasound exhibit a highly impacted surface and perforations of the visible membrane have been noticed. Moreover, compared to conventional extraction without use of ultrasound, a higher oil extraction yield has been obtained. Pore formation in the membrane caused by cavitation; hypothesis which is supported by the visualization of yeast's surface modification that could explain the higher yields reached.

2.5. Local shear stress

During irradiation of a solid-liquid mixture by ultrasound, some shear forces are generated within the liquid and at the vicinity of solid materials. Shear forces and turbulences result from the evolution (oscillation and collapse) of cavitation bubble within the fluid. Resulting streaming and acoustic micro-streaming effects are of interest in applications such as mixing or emulsification [35].

Regarding UAE, shear effects could explain some observations previously made [36], where oil enrichment in basil essential oil

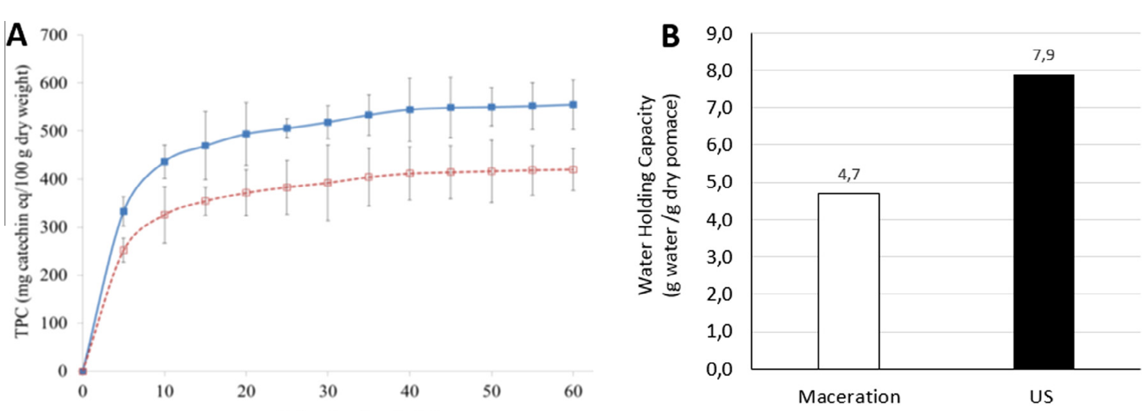

Fig. 4. Ultrasonic capillary effect induced by high power ultrasound on apple pomace. (**A**: Comparison of total polyphenol extraction (TPC) by maceration under agitation (●) and by ultrasound (ultrasound reactor 1 L, 25 kHz, ambient temperature) (●); **B**: Comparison of Water Holding Capacity of apple pomace after 10 min, for maceration under agitation and ultrasound (US probe, 20 kHz, ambient temperature)).

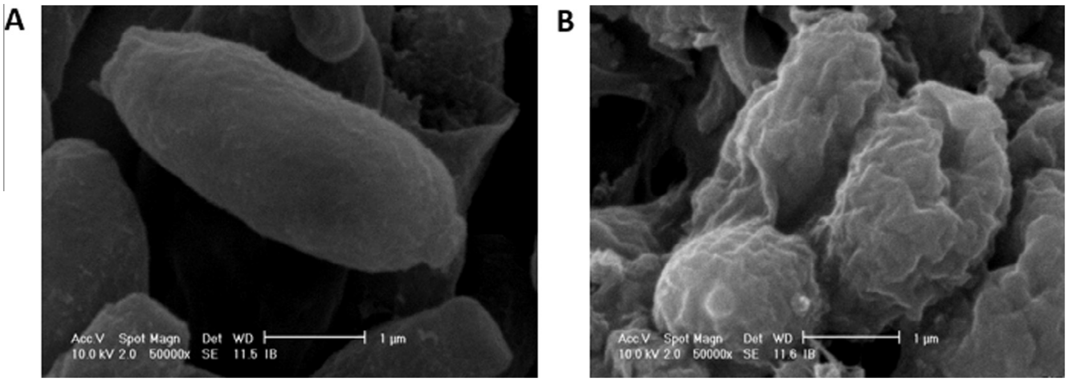

Fig. 5. Effect of power ultrasound on *Yarrowia Lipolityca* (**A**: SEM microscopy for control yeast; **B**: SEM microscopy for US-treated yeast).

was investigated. Basil leaves were submitted to ultrasound in olive oil (US reactor, 1L, REUS, ambient temperature). Extraction kinetics of eugenol, a representative terpene contained in basil essential oil is compared between UAE and maceration (Fig. 6-A). For eugenol extraction by UAE a direct solubilization is noted, whereas the extraction process seems more diffusive in the case of maceration. In basil, essential oils are contained in glands which are located at the surface of leaves (Fig. 6-C-1) [37]. For leaves treated by maceration in olive oil, the oil gland external envelop is still intact (image 2). In the case of leaves observed after an ultrasound irradiation, the oil gland seems to have exploded. It can be also noted that no other impact of ultrasound (e.g. pitting or erosion) is visible on the leaf, aside from the oil gland. It could be hypothesized that shear forces generated locally at the collapse of cavitation bubble close to the oil gland could cause its rupture. Another hypothesis could be that there is a pressure build-up within the gland or occurrence of cavitation inside the gland itself [38]. To assess this latter hypothesis, we compared the US power dissipation in olive oil and eugenol (Fig. 6-B). Temperature increase is higher with olive oil than with eugenol, which is due to a higher heat capacity for eugenol than for vegetable oil. Quantification of power dissipation (calculated according to Eq. (1)) is higher in eugenol than olive oil, which would indicate that cavitation occurring in essential oil could be more important than in olive oil.

2.6. Detexturation

In some cases after US extraction, a destruction or detexturation of plant structures has been observed. This effect has been noticed in a previous study on essential oil extraction from caraway seeds [39]. Total oil yields are similar between conventional extraction (reflux extraction with hexane) and UAE (US probe, 20 kHz), however a higher selectivity towards terpenes was noted for UAE (Fig. 7). Distinguishable physical modifications of caraways seeds

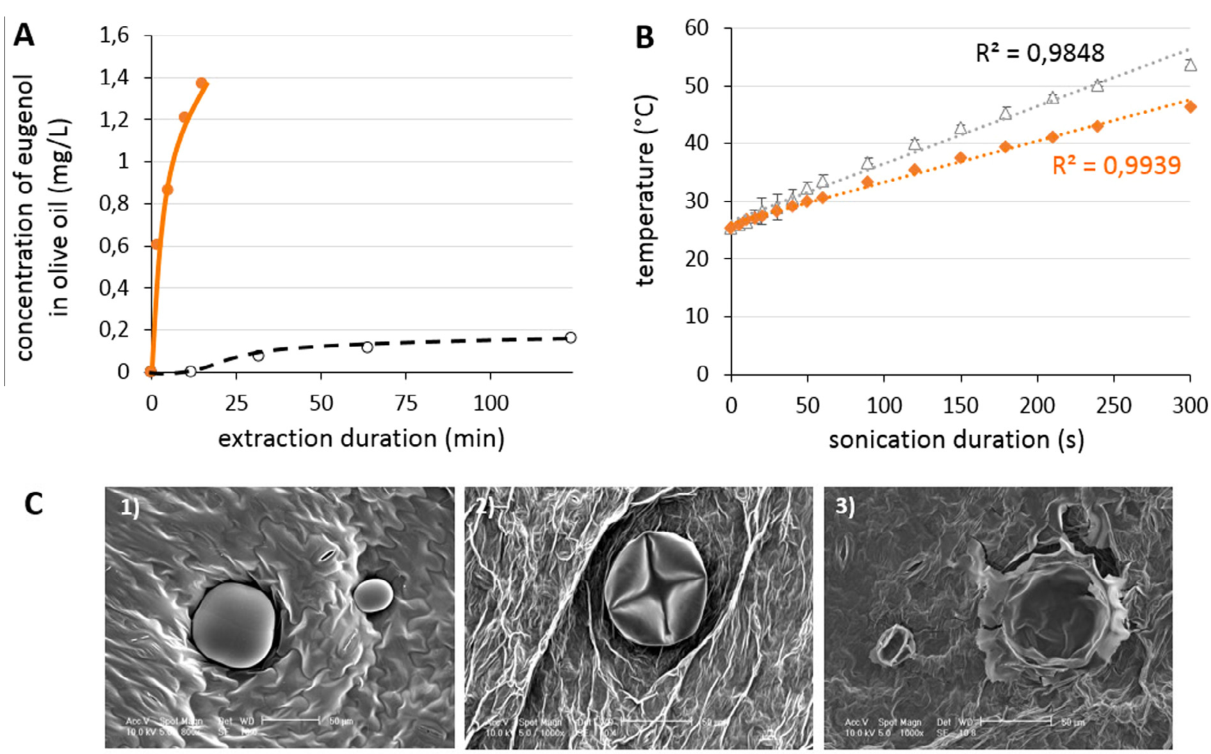

Fig. 6. Effect of power ultrasound on basil leaves. (**A**: Comparison of extraction kinetics of eugenol in olive oil for UAE, US reactor 25 kHz (●) and for maceration (○); **B**: US power dissipation during sonication for eugenol (◆) and olive oil (△); **C**: SEM microscopic observation of an essential oil gland, 1) control, 2) after maceration and 3) after UAE (US reactor 25 kHz)).

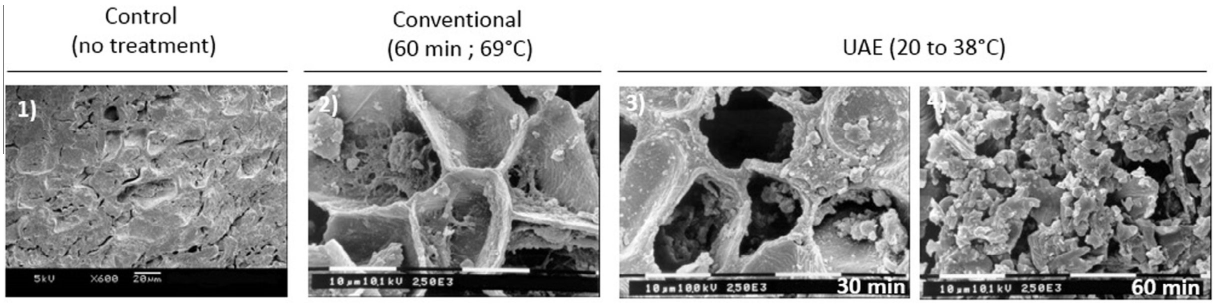

Fig. 7. Effect of power ultrasound on carvi seeds. (SEM microscopy for untreated seeds (1), seeds after conventional extraction (2) and UAE: US probe, 20 kHz after 30 min, (3) and after 60 min, (4)).

were noticed according to the extraction process used. Untreated seeds appear filled and intact. Observations of residual caraways seeds after conventional extraction and UAE at low temperature enable to identify different modifications (Fig. 7).

Conventional extraction leaves the cells structures intact but emptied due to transfer of cell content in the solvent. A gradual degradation of cell walls is obtained after ultrasound: at 30 min, cell walls are affected at various degrees and at 60 min of treatment, cells structures are totally broken and converted to undefined shapes (Fig. 7). It could be assumed that such cell disruption favored accessibility to the solvent. Such destruction or detexturation of cells structures is rarely reported after UAE, but some studies and reviews indicate a destructive effects on living cells and micro-organisms or enzymes [40].

2.7. Combined mechanisms

Overall, several mechanisms have been identified as acting on ultrasound assisted extraction: fragmentation, erosion, sonocapillary effect, sonoporation, local shear stress and destruction-detexturation of plant structures. Aiming at clarification, we chose to explicit and give evidence of each effect separately. However, during UAE a combination of effects most probably occurs. Also, perhaps these effects are sequential during the extraction process. Additionally, although not detailed as a mechanism, the intense mixing effect generated by the propagation of ultrasound in the liquid medium contributes to enhancement of mass transfer, greatly improving the solute transfer rate. The mixing effect at a macroscopic scale is due to acoustic streaming and at a local stage, acoustic microstreaming occurs [35]. Combining mixing effects to physical impacts of ultrasound on raw material may explain the enhanced extraction performances of ultrasound.

Comprehension of the possible mechanisms also points out that raw material has the major impact on extraction. Additionally, the type of pretreatment applied on the raw material to be treated will also contribute to extraction performances; e.g. milling, flaking, drying will affect the accessibility of the compounds to be extracted. A future trend could to identify if a generalization of ultrasound effect depending on the type of raw material could be obtained.

3. Influencing parameters of ultrasound assisted extraction

Sonochemical effects of ultrasound in a liquid are attributed to the acoustic cavitation phenomena [11]. In the ultrasound field, acoustic cavitation generally refers to bubble formation, growth and implosion occurring during the propagation of an ultrasound wave in a liquid media [41]. The molecules constitutive of the liquid medium are held together by attractive forces [42]. The propagation of an ultrasound wave through an elastic medium induces a succession of compression and rarefaction phases, which results in a longitudinal displacement of those constitutive molecules. The molecules forming the liquid phase are temporarily dislodged from their original position and during the compression cycles, they can collide with the surrounding molecules. During the rarefaction phases, a negative pressure will be exerted, pulling the molecules apart [42]. The extent of the negative pressure depends on the nature and purity of the liquid [10,42]. At a sufficient high intensity of a sound wave, during a rarefaction phase the attraction forces between them might be exceeded, generating a cavity in the liquid [10]. In a liquid, the cavities created into the medium are cavitation bubbles.

The cavitation bubbles are able to grow by coalescence, and/or rectified diffusion [43,44] since vapors or gas dissolved in the medium will enter the bubble during rarefaction phase and will not fully be expelled during the compression cycle. Cavitation bubbles are commonly classified in to two types: stable and transient [10,44]. Stable cavitation bubbles undergo many compression and rarefaction cycles and oscillate often non-linearly around an equilibrium size. The transient cavitation bubbles exist for one or at most for a few acoustic cycles, during which they expand very quickly to at least double their initial size before collapsing violently into smaller bubbles [10,44]. Although transient cavitation bubbles are considered as "active cavitation bubbles", Ashokkumar (2011) [43] highlighted that both types of bubbles are high-energy collapse bubbles.

When the size of these bubbles reaches a critical value, they collapse during a compression cycle and a transitory hot spot is created [45]. The collapse of cavitation bubbles generates extreme local conditions: determined temperatures up to approximately 5000 K [45] and estimated pressures around 50–1000 atm [11]. Hotspots created are able to accelerate dramatically the chemical reactivity of the medium [45,46].

When acoustic cavitation bubbles collapse near and onto the surface of a solid material, a number of physical effects are reported [11]. The collapse of the bubble generates high-speed jets of liquids into the surface and creates shockwave damages. Those effects can lead to fragmentation of friable materials and localized erosion. In the case of a solid-liquid slurry, the acoustic cavitation and shockwaves induce intense macro-turbulence, micro-mixing and subsequently interparticle collisions. It results from these factors an overall enhanced reactivity in the media and an increased mass transfer of solid particles due to reduction of particle size.

In this section, those parameters, which influence Ultrasound-Assisted Extraction (UAE), are detailed. The study of those parameters is of great importance in order to obtain a high extraction efficacy often resulting in obtaining the highest extraction yield. However, it is necessary to consider that the yield is not always the sole objective of an extraction process, but also the lowest use of non-renewable resources along with low energy consumption.

3.1. Physical parameters

As ultrasound is a mechanical wave, its characteristics such as frequency, wavelength and amplitude can influence the acoustic cavitation and therefore extraction. The influence of power input as well as the reactor design and shape of the probe can influence the process [47]. The impact of those parameters will be reviewed in this section.

3.1.1. Impact of ultrasound physical characteristics: power and frequency

The measurement of the actual applied acoustic power in a sonochemical process is not always reported, although some physical methods, which allow the direct or indirect measurement of the applied energy, are available. These methods estimate the transferred energy by measuring either chemical or physical changes on the medium when ultrasound is applied. The most common physical methods are the measurement of acoustic pressure using hydrophones or optical microscopes, the aluminum foil method and the calorimetric method [48–50]. And among the chemical methods, the indirect measurement of $OH^{\cdot}$ radicals formed by sonoluminescence or chemical dosimeters are also used [51,52]. As an example, to calculate the power by calorimetry, it is considered that the actual input power from the device is converted to heat which is dissipated in the medium. In this case, the effective ultrasound power is calculated according to Eq. (1) [53,54].

$$\mathrm{P} = \mathrm{m.Cp.}\frac{\mathrm{dT}}{\mathrm{dt}} \tag{1}$$

where Cp is the heat capacity of the solvent at constant pressure ($\mathrm{J.g^{-1}.{}^{\circ}C^{-1}}$), m is the mass of solvent (g) and dT/dt is the temperature rise per second.

Several studies show that high ultrasonic power causes major alterations in materials by inducing greater shear forces (depending on the nature and properties of the medium); however, in the food industry this parameter is usually optimized in order to use the minimum power to achieve the best results [55]. Generally, the highest efficiency of UAE, in terms of yield and composition of the extracts, can be achieved by increasing the ultrasound power, reducing the moisture of food matrices to enhance solvent-solid contact, and optimizing the temperature to allow a shorter extraction time. However, some studies showed the power variation can result in a certain selectivity of target molecules, where the ratio of some molecules is a function of the applied power [39,56]. US frequency may also impact on the extraction process and have to be chosen. The frequency will impact on the bubble resonance size. For example, the bubble characteristics are compared at 20 kHz and 500 kHz in Table 1.

The most commonly used frequencies in UAE processes are comprised between 20 kHz and 100 kHz. The use of higher frequencies for ultrasound assisted extraction has been investigated in only few studies. Toma et al. (2001) [12] noticed a reduced physical impact on the structure of marigold petals when applying high frequencies (500 kHz) compared to 20 kHz. Interestingly, Chukwumah et al. (2009) [58] report a selective extraction of some phenolics from peanuts according to the frequency applied: at 25 kHz (higher extraction of daidzein and genistein) and 80 kHz (biochanin A and trans-resveratrol). However, longer extraction durations where required when using the 80 kHz frequency. González-Centeno et al. (2014) [59] evaluated three frequencies (40 kHz, 80 kHz and 120 kHz) for the extraction of phenolics from grape pomace. Using the response surface methodology for the study of influencing parameters, the authors highlighted that 40 kHz was most effective.

As ultrasound frequency increases, the production and intensity of cavitation in liquid decreases [10]. At high frequency, the acoustic cavitation would be more difficult to induce since the cavitation bubbles need a delay to be initiated during the rarefaction cycle and cycles of compression-rarefaction can be too short to allow the increasing growth of the cavitation bubbles. The length of rarefaction phase (during which cavitation bubbles grow) is inversely proportional to ultrasonic frequency; therefore at high frequencies, larger amplitudes and intensities are required to generate cavitation [10].

At low frequencies, the transient cavitation bubbles are relatively less numerous although with high diameter, which privileges the physical effects instead of the chemical ones [44,60]. The effect of the frequency may be linked not only to the cavitation bubble size, but also to its influence on the resistance to mass transfer [61].

Table 1
Comparison of characteristic values at 20 kHz and 500 kHz for air saturated water at an ultrasonic intensity of 10 W/cm^2 (from Pétrier et al., 2008 [57]).

Frequency (kHz)	Amplitude (μm)	Acoustic pressure (atm)	Wavelength (cm)	Collapse duration (μs)	Average diameter of pulsating bubble (μm)
20	2.95	5.4	7.42	10	330
500	1.1	5.4	0.29	0.4	13

3.1.2. Intensity

Ultrasonic intensity is expressed as the energy transmitted per second and per square meter of emitting surface [8]. This parameter is directly correlated to the amplitude of the transducer and consequently to the pressure amplitude of sound wave [62]. With the increase in the pressure amplitude, bubble collapse will be more violent. To achieve cavitation threshold, a minimum value of UI is required. Regarding extraction, determination of ultrasonic intensity (UI) is a relevant input value impacting strongly on extraction efficiency. UI is calculated using the calculated power delivered to the media as shown in Eq. (2) [8].

$$UI = \frac{P}{S} \tag{2}$$

where UI is the ultrasonic intensity (W/cm^2), P is the ultrasound power (W) as calculated by the Eq. (2), and S is the emitting surface of the transducer.

The increase of UI generally results in an increase of sonochemical effects [10]. As increasing the amplitude can increase UI, it is important to note that high amplitudes can lead to rapid deterioration of the ultrasonic transducer, which results in liquid agitation instead of cavitation and in poor transmission of the ultrasound through the liquid media. However, the amplitude should be increased when working with high viscosity liquids such as oils [62].

Effect UI was evaluated at 16.4, 20.9 and 47.6 W/cm^2 at 20 kHz for soybean oil extraction [63]. The study shows an increase in yield up to 20.9 W/cm^2, beyond which no further increase is noted. A similar tendency was noted by Wang et al. (2015) [64], which study on UAE of pectin at 20 kHz indicate that UI (varied between 10.18 and 14.26 W/cm^2) should be subjected to an optimization, since the highest value of UI not leading to the highest yields. Therefore it seems that UI is a parameter that should be studied for optimization of UAE.

3.1.3. Shape and size of ultrasonic reactors

Since ultrasound waves are reflected when a solid surface is attained, in the case of extraction using an ultrasonic bath, the shape of the reaction vessel is critical. The best choice would be a flat bottom vessel such as a conical flask in order to attain a minimum reflection of waves [65]. The thickness of the vessel should also be kept to the minimal to reduce attenuation [62]. It is necessary to calculate the optimum reactor dimensions and the position of the emitter in relation to the transducer to attain maximum energy transferred to the medium [66]. Further advances have been made by taking into account the lack of homogeneity of the pressure field in the reactor in order to optimize the process efficiency [61,67]. Also, in the case of ultrasonic probes a rapid decrease of intensity is observed both radially and axially. For this reason a minimal space between the ultrasonic probe and the wall of the container must be respected, while ensuring that the probe does not touch the container to avoid damages on the material [62].

In the case of the use of an ultrasonic probe, the shape and diameter of this last one may have an influence on the extraction. The stepped probe gives the highest amplitude magnification (i.e., power, amplitude gain $(D/d)^2$) of the shapes shown. Nevertheless, the exponential probe shape offers small diameters at its working end, which makes it particularly suited to micro-applications [62].

Most of the probe emitters are composed of a titanium alloy, since this material is thermo-resistant and behaves well under corrosive conditions. However, the erosion of this material is often important, leading to transfer of metal particles into the extraction medium. Some new materials are investigated for ultrasound probe tips, such as quartz and Pyrex, which might solve the problem of metal particles release [68].

3.2. Medium parameters

The medium presents intrinsic characteristics that need to be taken into consideration in order to achieve the expected results in the extraction process assisted by ultrasound.

3.2.1. Solvent

Solvent choice in UAE is driven by the solubility of the target metabolites but also by physical parameters such as viscosity, surface tension and vapor pressure of the solvent. Those physical parameters will affect the acoustic cavitation phenomenon and more specifically cavitation threshold [10]. The initiation of cavitation in a liquid requires that the negative pressure during the rarefaction cycle have to overcome the cohesive forces between molecules composing the liquid. A rise of viscosity, or a rise of surface tension, induces an increase of these molecular interactions hence raising significantly the cavitation threshold. In this manner, the amplitude should be increased when working with samples of high viscosity. This is because as the viscosity of the sample increases so does the resistance of the sample to the movement of the ultrasonic device, for instance the tip of an ultrasonic probe. Therefore, a high intensity (or high amplitude) is advised in order to obtain the necessary mechanical vibrations that will result in cavitation [62]. A solvent with low vapor pressure is preferred in UAE, as the collapse of cavitation bubble is more intense compared to solvents with high vapor pressure [69]. However, vapor pressure depends on the temperature in the liquid medium.

3.2.2. Temperature

The temperature strongly impacts the solvent's properties. An increase of temperature results in a decrease of both viscosity and surface tension, and induces an increase of vapor pressure. A rise in vapor pressure causes more solvent vapors to enter the bubble cavity and numerous cavitation bubbles, which will collapse less violently and reduce sonication effects [62]. As a consequence, at higher temperatures, the sonochemical effects due to collapse of cavitation bubbles may be reduced. Therefore, sonochemical effects are favored by low temperatures and a control of temperature is usually applied to limit temperature rise [70].

For extraction processes, temperature contributes to efficiency of extraction. Usually, increase of temperature leads to an increase of extraction yield [71]. In the case of UAE, some authors report a beneficial effect of temperature rise from 20 °C to 70 °C compared to non-sonicated extractions [7]. This effect has been justified by an increase in the number of cavitation bubbles and a larger solid-solvent contact area, enhancements of solvent diffusivity with consequent enhancement of desorption and solubility of the interest compounds. However, this effect is decreased when the temperature is near the solvent's boiling point and most authors report a beneficial effect of low temperature (below 30 °C) in the case of UAE [61,72,73]. It is important to choose an extraction temperature according to the target compound of extraction [74,75]. Hence, a temperature control is necessary to prevent the degradation of thermolabile compounds. The optimization of temperature parameter can be performed in order to obtain the highest yield of the target compounds without degradation, since this parameter can vary depending on the type of product.

3.2.3. Presence of dissolved gases and external pressure

The absence of gases renders formation of cavitation bubbles difficult, since cavitation bubbles are formed from gas (vapors) dissolved in the liquid [57]. Dissolved gases into the solvent act as nuclei for a new cavitation bubble [10,44]. However, application of ultrasound tends to degas a liquid. A gas bubbling can be used to control composition of cavitation bubbles and can affect sonochemical effects [10]. Generally, in the field of extraction, the composition of gases dissolved in the solvent is not controlled.

If external pressure is increased, then a greater acoustic pressure is required to induce cavitation. But once the cavitation threshold is reached under external pressure (>1 atm), the intensity of the cavitation bubble collapse is higher than without pressure and consequently, an enhancement in sonochemical effects is obtained [44,62].

3.2.4. Matrix parameters

Depending on the objective of the UAE and the target molecules, plant matrix could be used either fresh (e.g. algae, yeast...) or dry (e.g. herbs, oleaginous seeds...). The pre-treatment of the matrix is important and can impact extraction efficiency [24]. The solubility and stability of the target compounds in the chosen solvent and temperature of the liquid medium can influence the final yield of the extraction. Likewise, since the extractive system is a heterogeneous and complex porous media, the size of the cavitation bubble has an effect on the efficiency on the extraction. Other parameters related to the solid-liquid extraction such as the solid/liquid ratio and particle size of the material are relevant to the efficacy of extraction. The extraction yields may vary also due to plant material's structure, plasticity or compositional differences which will result in different degrees of impacts from cavitation effects [35].

4. Ultrasound techniques for extraction

4.1. Conventional techniques

High power ultrasound can be applied using two types of devices, ultrasonic bath or probe-type ultrasound equipment. Both systems are based on a transducer as a source of ultrasound power. The piezoelectric transducer is the most common type used in the majority of ultrasonic reactors. The ultrasonic bath is the most commonly known type of ultrasonic device usually consists of a stainless steel tank with one or more ultrasonic transducers.

Ultrasonic baths usually operate at a frequency of around 40 kHz and can be equipped with temperature control. They are readily cheap, available and large numbers of samples can be simultaneously treated. However, compared with probe systems, the low reproducibility and low power of ultrasound delivered directly to the sample are major drawbacks. Indeed, the delivered intensity is highly attenuated by the water contained in the bath and the glassware used for the experiment. Recently a new bath system reactor has been developed by REUS (Contes, France) operating at 25 kHz, which is mostly used for extraction applications. It consists in a stainless steel reactor equipped with a double-layered mantle with water circulation to allow temperature control with cooling/heating systems.

High power ultrasonic probes are generally preferred for extraction applications. The probe system is more powerful due to an ultrasonic intensity delivered through a smaller surface (only the tip of the probe), when comparing to the ultrasonic bath. They are generally operated at around 20 kHz and use transducer bonded to probe which is immersed into the reactor resulting in a direct delivery of ultrasound in the extraction media with minimal ultrasonic energy loss. There are several designs of probes with different lengths, diameters and tip geometries. The probe selection is made according to the application and to the sample volume to be sonicated. The intensity of ultrasound delivered by the probe system to the liquid media induces a quick increase of temperature in the reactor. The cooling of the reactor by a double-jacket is then required to conduct extraction. The manufacturers of high-power ultrasound equipment have been focusing on designing devices which include specific operational features such as continuous flow mode. The equipment basically consists of a glass or stainless steel reactor, through which the fluid mixture is pumped at atmospheric or high pressure to conduct mano-sonication. The continuous reactor could be cooled or heated with a double mantle to conduct mano-thermo-sonication (D, Fig. 8).

4.2. Hybrid techniques: combination of ultrasound with conventional methods

4.2.1. Sono-soxhlet: ultrasound assisted soxhlet extraction

Fats and oils are traditionally extracted from their matrix using the Soxhlet extraction. Invented in 1879, this apparatus has been widely used in various fields such as environmental applications, foodstuffs and also pharmaceutics. Its principle is relatively easy and proceeds by an iterative percolation of condensed vapors of a boiled solvent, generally n-hexane. Nevertheless, Soxhlet extraction has some disadvantages such as a long operation time (several hours), large solvent volumes, evaporation and a concentration step needed at the end of the extraction. There are only few

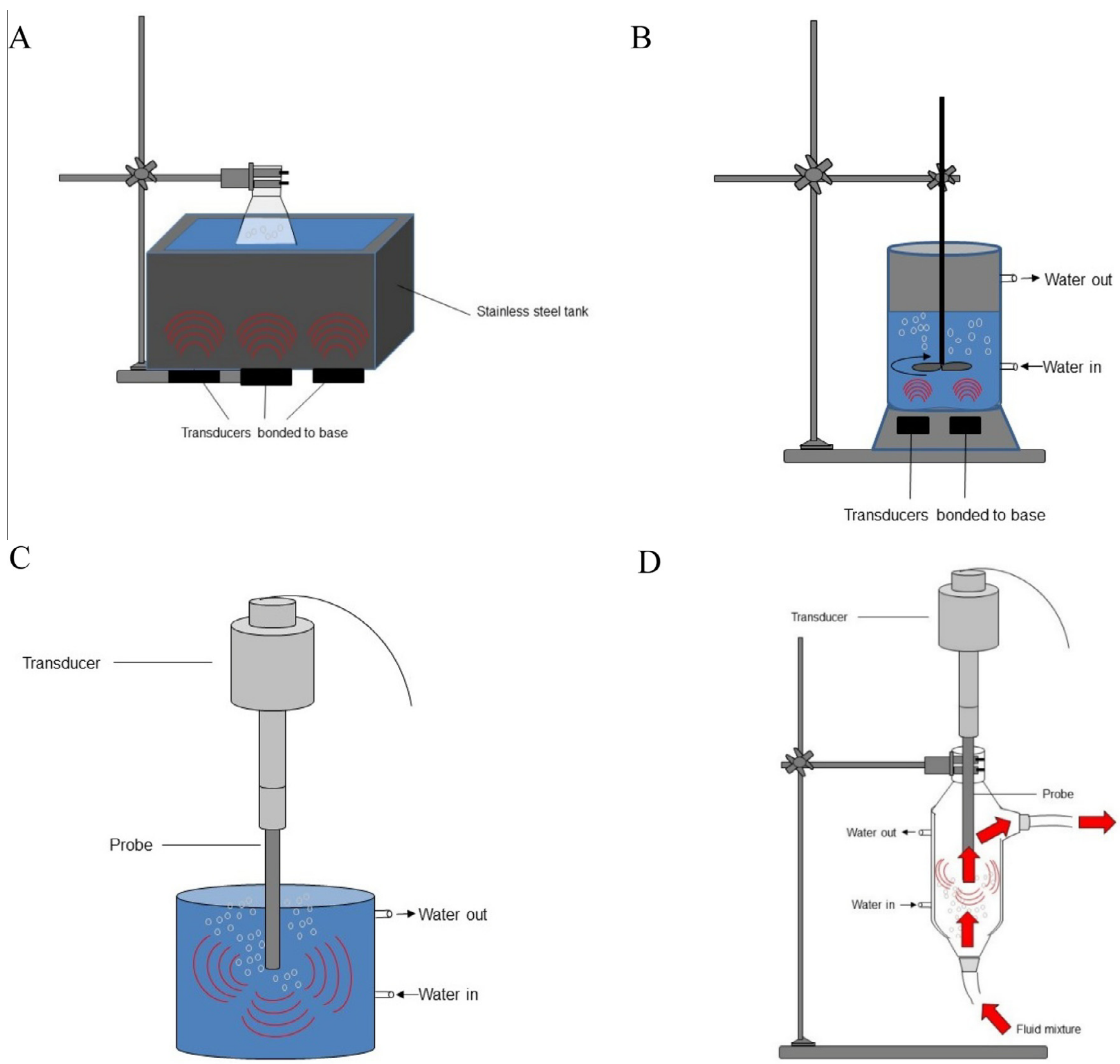

Fig. 8. Commonly used ultrasonic systems (A: Ultrasound bath, B: Ultrasound reactor with stirring, C: Ultrasound probe, D: Continuous sonication with ultrasound probe).

processes in the literature that have reported the combination of Soxhlet extraction with innovative techniques, such as ultrasound, for the acceleration of fat and oil extraction.

The teams of Luque de Castro and Chemat [76,77] developed original Sono-Soxhlet methods. Ultrasound is applied outside or inside the extraction chamber to enhance the solid liquid extraction and migration of metabolites from solid matrix to solvent (Fig. 9 a and b). Sono-Soxhlet combines the advantages of the extraction performed with Soxhlet (extraction repeated by a fresh solvent) and enhancing mass transfer with ultrasound (reduction of extraction time). The process ensures the complete, rapid and accurate extraction of the samples. This system has been also been used for the extraction of the oil content and the fatty acid composition of oleaginous seeds, lipids from sausage products, fat from cheese and bakery products.

4.2.2. Sono-clevenger: ultrasound assisted clevenger distillation

The traditional method used to isolate volatile compounds as essential oils from plant material (herbs, spices, barks, fruits...) is alembic distillation that, in chemistry laboratories, is also called Clevenger distillation. This method proceeds by the iterative distillation and boiling of the aromatic matrix, it generally uses large quantities of water and energy. The extraction time can vary from 6 to 24 hours. During distillation, fragrant plants exposed to boiling water or steam, release their essential oils through evaporation. Recovery of the essential oil is facilitated by distillation of two immiscible liquids, namely, water and the essential oil. This is based on the principle that, at the boiling temperature, the combined vapor pressures equal the ambient pressure. Thus the essential oil ingredients, for which boiling points normally range from 200 to 300 °C, are evaporated at a temperature close to that of water. As steam and essential oil vapors are condensed, both are collected and separated in a vessel traditionally called the "Florentine flask". The essential oil, being lighter than water, floats at the top while water goes to the bottom and is separated.

With growing a flavour and fragrance industry and the increasing demand for more natural products, the need for novel extraction methods has become more intense. The combination of ultrasound with Clevenger or alembic distillation has attracted growing interest in the past few years. This has resulted in the development of Sono-Clevenger [78] specifically aimed for obtaining essential oils from plant materials. Sono-Clevenger is an original combination of ultrasound cavitation and Clevenger distillation at atmospheric or reduced pressure (Fig. 9 c and d). It provides yields comparable to those obtained by traditional hydrodistillation but with reduced extraction times and enhanced yields. The

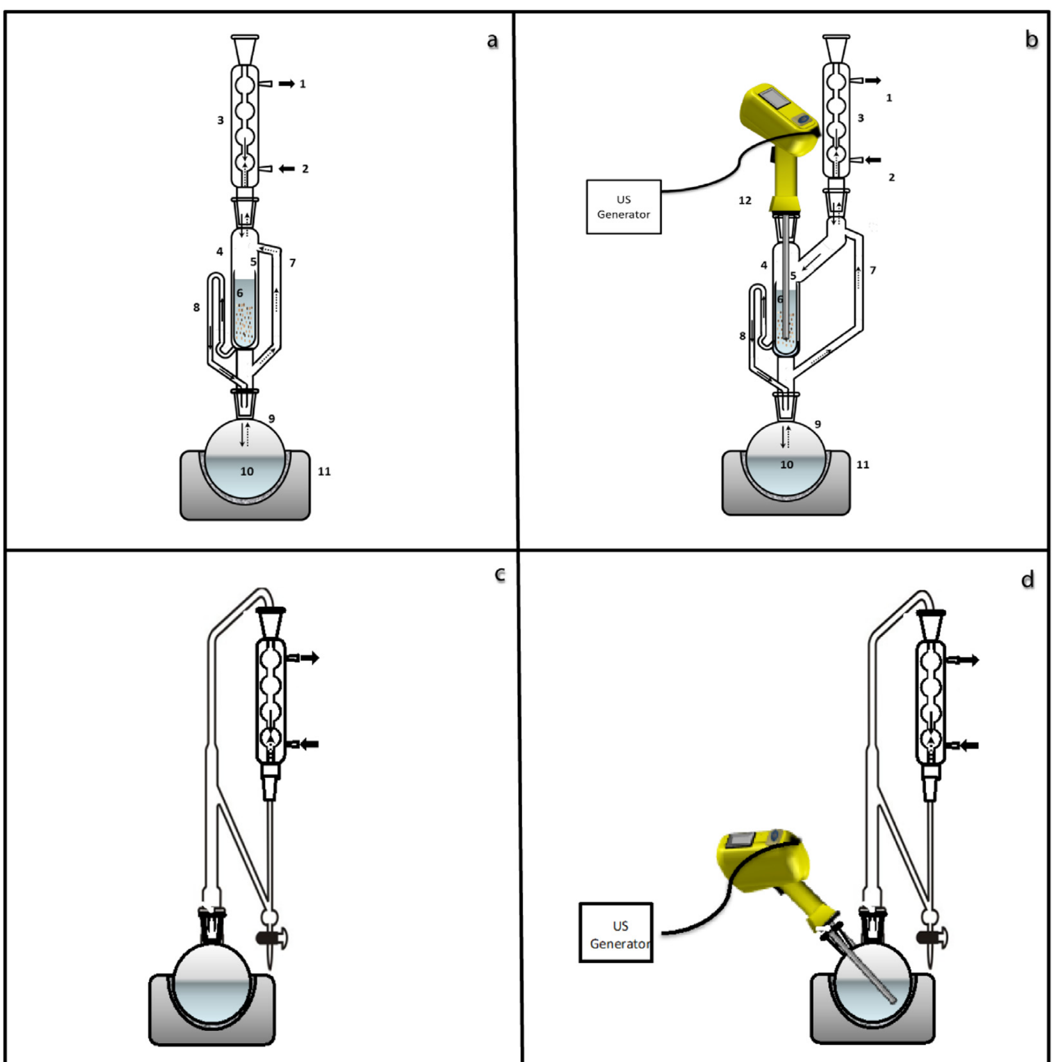

Fig. 9. Hybrid extraction techniques ((a) conventional Soxhlet, (b) Sono-Soxhlet, (c) conventional Clevenger, (d) Sono-Clevenger).

thermally sensitive crude materials seem to be preserved with this method, in contrast to conventional Clevenger distillation.

4.3. Combination of ultrasound with innovative techniques

4.3.1. Combination of microwave and ultrasound

The combination of ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE) by means of simultaneous irradiation (UMAE) is one of the most promising hybrid techniques for fast, efficient extractions. Since the pioneering work of Cravotto et al. [68], several applications of combined US/MW irradiation for plant extraction have appeared in the literature, the great potential of this hybrid technique has not yet been adequately exploited (Fig. 10 a). Due to the high efficiency and the dramatically short extraction time, we believe that UMAE has a great potential for academic and industrial research activity. It is a cost-effective extraction technique for fast sample preparation and a new strategy for process intensification. If, on one hand, double simultaneous irradiation can bring additive or even synergic effects to the extraction phenomenon of vegetal matrices, on the other, non-metallic horns can only be used at moderate power. As described by Cravotto and Cintas [79], Pyrex®, quartz or Peek® made horns can be safely used up to 90 W, above that the intrinsic structure of the material can be irreversibly damaged. This is however a minor limitation because UMAE requires lower power levels than the two single energy sources alone. Ultrasound can dramatically improve the extraction of a target component mainly through the phenomenon of cavitation. The mechanical ultrasonic effect promotes the release of soluble compounds from the plant body by disrupting cell walls, enhancing mass transfer and facilitating solvent access to cell content. Meanwhile, MW heats the whole sample very quickly inducing the migration of dissolved molecules. The simultaneous irradiation increases solvent penetration into the matrix, facilitates analyte solvation and usually increases the solubility of target compounds.

UMAE has been successfully employed by Cravotto and Binello [80] as a complementary technique in the extraction of oils from vegetable sources; *viz*., soybean germ and a cultivated seaweed rich in docosahexaenoic acid (DHA).

4.3.2. Combination of DIC process and ultrasound

The Instantaneous Controlled Pressure Drop process, abbreviated DIC according to the French expression "Détente Instantanée Contrôlée". DIC extraction is based on fundamental studies concerning the thermodynamics of instantaneity. It involves a thermo-mechanical processing induced by subjecting the product

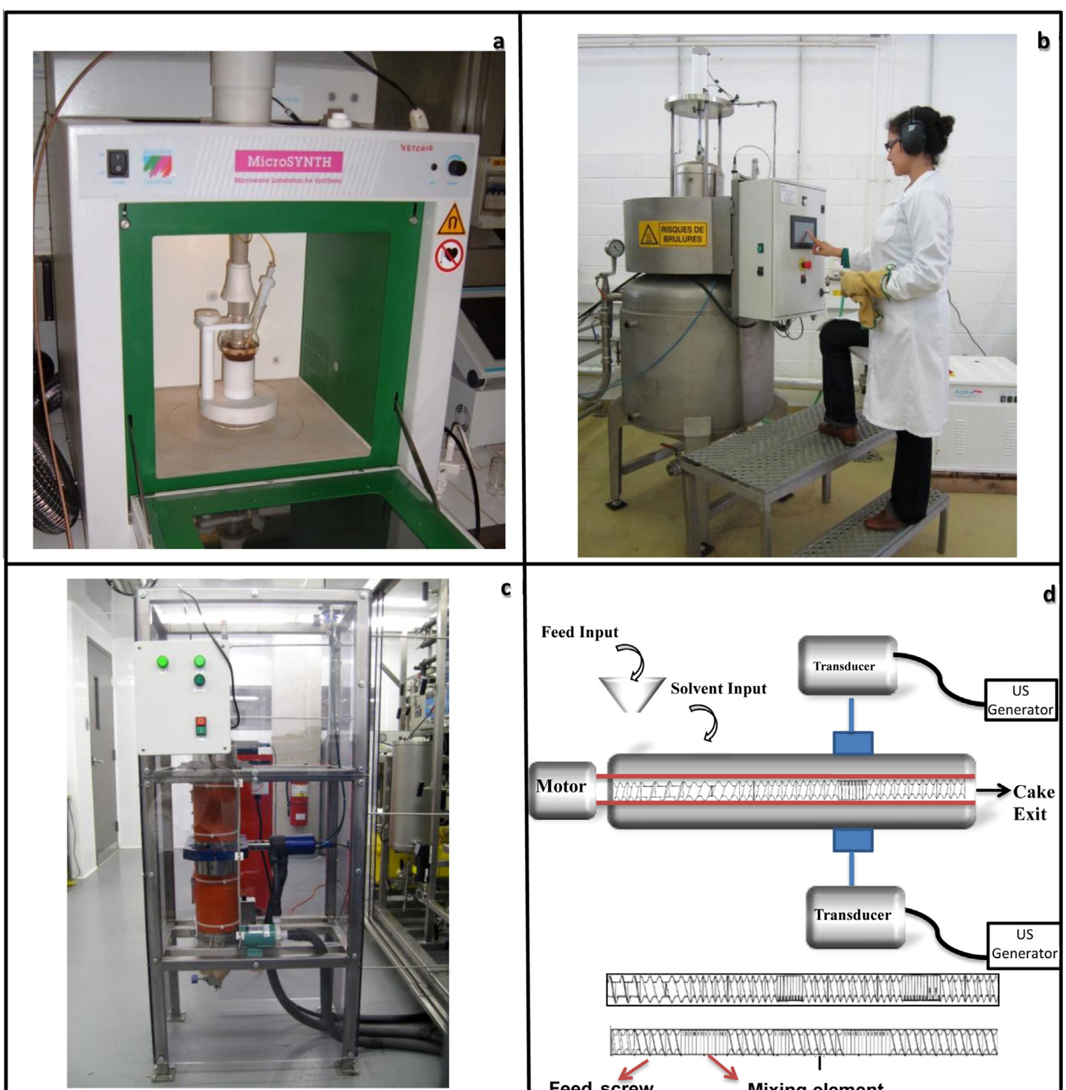

Fig. 10. Combined innovative extraction techniques ((a) ultrasound-microwave, (b) ultrasound – DIC, (c) ultrasound-SFE, (d) ultrasound-extrusion).

to a fast transition from high steam pressure to vacuum. DIC extraction usually starts by creating a vacuum condition, followed by injecting steam into the material for several seconds, proceeding then to a sudden pressure drop towards vacuum (about 5 kPa with at a rate higher than 0.5 MPa/s). By suddenly reducing the pressure, rapid auto-vaporization of the moisture inside the material will occur. It will swell and lead to texture change, which results in higher porosity as well as increased specific surface area and reduced diffusion resistance.

The combination of these two innovative techniques, cavitation (US) and mechanical (DIC), and their application to physical processes like extraction appears to be interesting (Fig. 10 b). However, it is not known how simultaneous US-DIC action could bring about a physical effect. Therefore, it is expected that the kinetics of the extraction processes will improve, but also it is thought that a new effect may occur. For instance, the high pressure level induced by DIC and the difference between internal and external pressure (controlled by Darcy law) could induce particle fragmentation and exudation, and ultrasound cavitation could induce fragmentation and erosion of solid particles and also induce enhanced mass transfer from the inside to the outside of the treated matrix. A combination of DIC (pressure phenomena) and ultrasound (cavitation) has been successfully applied to extraction with yield enhancements and a reduction in treatment time [81]. The sequential use of DIC and ultrasound assisted extraction triggered complementary actions materialized by supplementary effects. These effects can be illustrated through an example where sequential extraction of essential oil and antioxidants was made.

The impact of process combination on extraction was evaluated by comparison to two standard processes: hydrodistillation (HD) and solvent extraction (SE). First, the extraction of orange peel Essential Oil (EO) was achieved by HD during 4 h and DIC process (after optimization) during 2 min; EO yields was 1.97 mg/g dry material (dm) with HD compared to 16.57 mg/g dm with DIC. In the second part of the study, the solid residue was recovered to extract antioxidant compounds (naringin and hesperidin) by SE and UAE. Scanning electron microscopy of the residues showed that, after HD the recovered solid shriveled as opposite to DIC treatment which expanded the product structure. After 1 h of extraction, DIC treated orange peels with UAE extracts contained 0.825 ± 0.016 g/g of dm for hesperidin and 0.0645 ± 0.0002 g/g dm for naringin compared to 0.640 ± 0.027 g/g dm and 0.057 ± 0.002 g/g dm, respectively with SE. By combining DIC to UAE, it was possible to enhance kinetics and yields of antioxidant extraction.

4.3.3. Combination of ultrasound and supercritical fluid extraction

Supercritical fluid extraction (SFE) is a relatively recent extraction technique based on the enhanced solvent power of fluids above their critical point. Its usefulness in extractions is due to the combination of gas-like mass transfer properties and liquid-like solvating characteristics with diffusion coefficients, which are higher than those of a liquid. The majority of SFE studies have focused on the use of CO_2 because it is non-toxic, non-flammable, cheap, easily eliminated after extraction and endowed with a high solvating capacity for non-polar molecules. The major advantages of SFE include pre-concentration effects, cleanness and safety, higher yields, expeditiousness and simplicity. The drawbacks of SFE are the need for more expensive equipment and the difficulty of extracting polar molecules without adding modifiers to CO_2. Indeed, ultrasound permits the extraction of a wide variety of compounds using polar or non-polar solvents and much simpler equipment. When combined with supercritical fluid extraction, US enhance the mass transfer of the species of interest from the solid phase to the solvent used for extraction (Fig. 10 c) [82].

4.3.4. Combination of ultrasound and extrusion extraction

For the production of sugar, wine and fruit juices, or the dehydration of biological wastes and in vegetables oil industries, extraction is realized by pressing and extrusion. The pressing phase is composed of a compression step to exude a fluid containing the target metabolites from the porous matrix. The cells of fruit and vegetable tissues are surrounded with membranes and closed by a cell wall embedded into a middle lamella. The rigid wall components prevent easy damage of the membranes, and thus limit efficiency of the pressing extraction. The combination of pressing with other processes such as ultrasound can be studied in a research context, in order to obtain better extracts (quality and quantity versus time) at the stage of process intensification (Fig. 10 d). In general, the average extrusion force decreases with an increase in ultrasound amplitude resulting in better extrudability [83,84].

5. Protocols and applications

5.1. Fruits and vegetables

Fruits and vegetables are frequently used for the extraction of various molecules of interest such as antioxidants, pigments, lipids, phytochemicals and aromas, intended for direct or indirect applications in food, pharmaceutical and cosmetic industries. Fruits and vegetables contain a wide range of secondary metabolites in pulp, peel, seeds, and bark. Table 2 presents some applications of the use of ultrasound for the extraction of different kind of compounds from various fruits and vegetables. Antioxidants are able to prevent the oxidation process by reacting preferably with oxidizing agent instead of the target cells or molecules of interest [85]. Nowadays, there is a need in cosmetic, pharmaceutical and food industries to replace synthetic substances such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) which have shown some negative side effects on health [86]. Isolation and purification of natural antioxidants from natural plants is a critical step due to the co-extraction of undesirable by-products such as pigments, oils, waxes from matrices.

Conventional techniques for antioxidants extraction are maceration and Soxhlet extraction, which are time-consuming and require large volume of solvent [87]. Pan et al. [88] have reported a comparison between UAE and conventional extraction of antioxidants from pomegranate peel. For the both extraction processes, pomegranate marc was obtained after the juice processing of pomegranate fruit, then dried at 40 °C and ground using a hammer mill to achieve a particle size less than 40-mesh. Conventional maceration was performed using a water/peel ratio of 50/1 (w/w). Maceration was done with agitation (magnetic stirring at 1200 rpm) and was performed following a kinetic of extraction of 2–90 min at room temperature. Concerning UAE, ultrasound probe with area of 1.267 cm^2 and intensity levels between 2.4 and 59.2 W/cm^2 was used at constant frequency of 20 kHz. The sample container was kept constant at 25 °C, and covered by an aluminum-foil paper to prevent photo-oxidation. The performances of UAE were performed in continuous and pulsed modes with total extraction times of 2, 10, 20, 30, 60, and 90 min, as being during conventional extraction. The optimal condition obtained for UAE was 59.2 W/cm^2 for intensity level and an extraction time of 60 min. Sonication with pulse duration of 5 s and a resting interval of 5 s permitted to improve the antioxidant yield by 22% and reduced extraction time by 87%, and continuous UAE allowed to increase the yield by 24% and reduced the extraction time by 90%, compared to conventional maceration. In brief, the use of ultrasound enable to intensify and largely maximize the yield of extraction and antioxidant activity, while decreasing energy consumption and extraction time. Hammi et al. [89] has also

Table 2
Applications of UAE in the extraction of compounds from fruit and vegetables.

Matrix	Extract	Processing device	Experimental conditions	Reference
Pomegranate peel	Antioxidant	US probe (20 kHz, 1.267 cm^2)	Pulse = 5 s on, 5 s off IP = 59.2 W/cm^2 T = 25 °C t = 60 min ratio: water/peel, 50/1 (w/w)	[88]
Zyzyphus lotus fruit	Antioxidant	US bath (360 W)	Pulse = 2 s on, 2 s off T = 63 °C t = 25 min ratio solvent/solid: 67 mL/g Solvent: ethanol (50%)	[89]
Tomato pomace	Carotenoids (all-trans-lycopene, β-carotene)	US probe (20 kHz, 13 mm)	A = 58–145 µm T = 25 °C t > 10 min m = 3 g, V = 100 mL Solvent: hexane/ethanol (50:50, v/v)	[90]
Pomegranate (*Punica granatum*) rinds	Natural color	US probe (20 kHz)	P = 80 W T = 25 °C t = 30 min to 3 hours m = 1 g, V = 50 mL solvent: water	[91]
Jabuticaba (*Myrciaria cauliflora*) peel	Phenol (ellagic acid), anthocyanin (cyaniding-3-O-glucoside)	US bath (25 kHz, 150 W, 2.7 L)	T = 30 °C t = 10 min Solvent: ethanol:water (pH = 1) Ratio: 46% (v/v)	[93]
Garlic (*Allium sativum*) cloves	Aroma	US bath (35 kHz)	T = 25 °C t = 30 min 3 times extraction (V = 50 mL) Solvent : diethyl ether, hexane, ethyl acetate	[92]
Grape (*Vitis vinifera*) seeds	Phenol, antioxidants, anthocyanins	US bath (40 kHz, 250 W, 10 L)	T = 33–67 °C t = 16–34 min m = 2 g, V = 100 mL Solvent: ethanol Ethanol concentration: 33–67%	[94]

demonstrated the efficacy and absence of degradation for ultrasound-assisted extraction of antioxidant from *Zyzyphus lotus* fruit. The optimum operating conditions reported by the author was ethanol concentration of 50%, extraction time of 25 min, extraction temperature of 63 °C for reach a high phenolic content of 40.78 mg gallic acid equivalent/g dry matter and DPPH activity of 0.289 mg/mL.

The use of ultrasound has also been proved as a promising technology to extract carotenoids from tomato by-product (skin, seeds, and part of the pulp) [90]. Ultrasound significantly increased the extraction yield of 143% in comparison with conventional extraction and did not cause any degradation of carotenoids. Sivakumar et al. [91] has reported the significant improvement (13–100%) of the extraction yield of the natural colors obtained from different plant materials. Kimbaris et al. [92] have demonstrated that the use of ultrasound for essential oil extraction from garlic reduced the degradation of thermal-sensitive molecules, compared to hydro-distillation.

5.2. Herbs and spices

Herbs and spices are commonly used for food, cosmetic or pharmaceutical applications as sources of various compounds of interest such as antioxidants, capsaisinoids, aromas, flavors, fragrances or volatile compounds that can be extracted from different matrices such as pepper, rosemary or caraway seeds for example. Ultrasound can successfully be applied in the recovery of aroma molecules which are conventionally extracted by hydro-distillation [95] from a large range of herbs and spices using a Clevenger-type system at lab scale [96]. Flavors and fragrances are complex mixtures of volatile compounds which consist in complex mixtures of mono- and sesquiterpene hydrocarbons, and oxygenated materials biogenically derived from them [97].

Assami et al. [98] describe the use of ultrasound for aromas recovery where a US-assisted Clevenger (or sono-clevenger) is compared to conventional Clevenger for the extraction of aromas from caraway seeds. Both extraction procedures are given hereafter: conventional extraction is performed using 150 g of seeds finely ground to 18.0–250 µm size in electric grinder for 20 s at a speed of 20,000 rpm using a cooling water system in order to prevent volatile loss during milling. The resulting mixture is then submitted to hydro-distillation for three hours. For US-assisted system a 3L double jacketed reactor composed of an inox jug (23 cm × 13.7 cm) and operating at a frequency of 25 kHz and at an intensity of 1 W/cm^2 was used. The mixture was homogenized thanks to a rotating pale and US was then applied for 30 minutes. For each experiment the mixture composed of 150 g of crushed material with 1.5 L of water (same ratio as the conventional extraction) was placed into the reactor and after the US treatment the resulting mixture was submitted to a Clevenger hydrodistillation for the recovery of the essential oil. Both extracts are qualitatively and quantitatively analyzed by GC–MS and a selectivity is noticed; the ultrasonic treatment has a clear influence on the recovery of carvone and limonene when compared to untreated seeds.

Other compounds such as capsaicinosids (noridihydrocapsaicin, capsaicin, dihydrocapsaicin, homocapsaicin, and homodihydrocapsaicin) can be extracted from pepper (*Capsicum frutescens*) and by changing solvent in the US-assisted extraction, selectivity has been observed among those compounds [99,100]. The possibility of selecting the compound of interest by US-assisted extraction can be observed for caraway seeds, as described before, where at low temperatures, a selectivity is observed for carvone extraction instead of limonene [39,98]. It can also be observed for US-assisted extraction of rosemary where carnosic acid is better extracted from dried material in ethanol, while rosmarinic acid is better extracted using methanol as solvent [101,102]. Several applications of the use of UAE for different target compounds from several herbs and spices are given in Table 3, with the UAE conditions.

5.3. Oleaginous seeds

Oleaginous plant seeds are a renewable resource available worldwide. Soybean alone represents over 70% of world production, followed by sunflower and rapeseed representing approximately 15% each. In Europe the most cultivated is rapeseed far ahead sunflower, soybean and also flaxseed taking an honest share in France. Oleaginous seeds can also be found in fruits (nuts, almonds, papaya seeds, fruits kernels) [107].

Fats and oils are a main source of energy used by the body. Moreover, they participate in the transmission of nerve impulses, maintain the integrity of cell membranes, have a role in cellular transport, and are precursors of many hormones. From all sources of lipid, oil seeds are complex matrices from which it is possible to extract monoacyl glycerols (MAG), diacyl glycerols (DAG), triacyl glycerols (TAG), and free fatty acids (FFA) associated with other minor compounds, also called micronutrients, such as pigments, sterols, antioxidants, alkaloids [108]. Oils are usually analyzed by GC-FID, after transmethylation of acylglycerols, in order to determine their fatty acid profile and investigations on minor components are generally conducted with HPLC analysis.

The conventional methods for seed oil extraction are hot or cold pressing like for flaxseed, solvent extraction (Soxhlet), and eventually combination of processes like for rapeseed. Pressing is an old technique to squeeze the oil out of solid residue [109], nevertheless matrix containing more than 30% oil, such as rapeseed containing nearly 50%, require more than a simple pressing to recover the maximum oil contained in the seed. A first prepressing is realized in order to remove part of the oil from the matrix, press-cake is then subjected to solvent extraction [109]. Industrially, solvent extraction step is generally performed in countercurrent extractors using large amounts of hexane.

Conventional Soxhlet extraction [110] is performed according international standard NF EN ISO 659 [111]. Ultrasound has successfully been applied to the Soxhlet extraction using a sono-soxhlet [76,77]. As for conventional Soxhlet, the sample is weighed and placed in the cellulose thimble plugged with cotton and placed in the extraction chamber. The Soxhlet apparatus is then placed into a thermostated water-bath. The sonicator probe is placed at 1 mm from the surface of the Soxhlet chamber with an inclination angle of 45° with respect to the vertical position and at 9 cm height from the bottom of the water bath. The extraction program consist of a number of cycles that depends on the extraction kinetics of the target compound. Each cycle involves three steps: (1) filling of the Soxhlet chamber by solvent evaporated from the distillation flask, condensate in the refrigerant, and dropped on the sample; (2) ultrasound irradiation of the cartridge for 10 s (duty cycle 0.5 s, output amplitude 40% of the nominal amplitude of the converter, applied power 100 W); (3) unloading of the Soxhlet chamber content after the solvent extraction reach the siphon height. After the extraction, the content of the flask is evaporated under reduced pressure. Several applications of the use of US for the extractions of compounds, mostly oil, from several oleaginous seeds are given below, in Table 4, with the UAE conditions.

5.4. Microorganisms

Microorganisms such as bacteria, yeast, fungi, and microalgae are able to produce primary and secondary interesting metabolites as pigments, antioxidants, polysaccharides, acids, lipids employed for cosmetic, food, pharmaceutic and biofuel applications. In oleaginous microorganisms, lipids are found mainly in the form of neutral lipids, glycolipids, phospholipids, and free fatty acids (FFA) [115]. Some strains with optimized culture conditions are able to content up to 70% w/w on dry biomass weight basis [116], thus are recognized as a promising source of feedstock for biodiesel production. Conventional methods used for lipid extraction from oleaginous microorganisms involve organic solvent extraction using non-polar or low polar solvents such as chloroform or hexane [117].

The most cited reference method for lipid extraction from biological materials is Bligh and Dyer [118]. It is an economical adaptation of the Folch procedure [119] which consists in a mixture of chloroform and methanol, forming a monophasic solvent system, to extract and dissolve the lipids. Adam et al. [120] have reported a study on an innovative technique such as solvent-free ultrasound-assisted extraction for lipid recovery from fresh *Nannochloropsis oculata* microalgae biomass in comparison with the conventional extraction methods. The conventional procedure for

Table 3
Applications of UAE in the extraction of compounds from herbs and spices.

Matrix	Extract	Processing device	Experimental conditions	Reference
Rosemary	Antioxidants (carnosic acid, ursolic acid)	US bath US reactor (150 W) US probe (1 kW)	S/L ratio = 1/20 (m/V), Solvent = EtOH/H_2O, 90/10 (V/V), t = 30 min, T = 40 °C	[103]
Pepper	Capsaisinoids	US bath (360 W)	m = 0.2–2 g, V = 15–50 mL, solvent = MeOH, EtOH, acetonitrile, MeOH/H_2O (0–100%), t = 2–25 min, T = 10–60 °C	[99]
Caraway seeds	Carvone, limonene	US reactor (25 kHz)	I = 1 W/cm^2, m = 150 g, V = 1.5 L, solvent = water, t = 30 min, Hydrodistillation	[98]
Marjoram	Antioxidants (rosmarinic acid, carnosic acid, luteolin-7-O-glucoside, apigenin-7-O-glucoside)	US probe (20 kHz, 19 mm)	m = 0.5 g, V = 25 mL, solvent = MeOH/H_2O 80/20 (V/V), t = 5–15 min, T = 15–35 °C, pulse = 5 s on, 5 s off	[104]
Saffron	Volatile compounds	US bath	M = 50 mg, V = 1 mL, solvent = MeOH/acetonitrile 38/62, (V/V), t = 22 min	[105]
Spearmint (*Mentha spicata*)	Flavor volatile compounds	US probe (200 W)	Amplitude = 25%, m = 50 g, V = 100 mL, solvent = EtOH/H_2O 70/30, (V/V), t = 5,10,15 min, T < 40 °C	[97]
Tea	Aroma compounds	US bath (40 kHz, 250 W)	m = 3 g, V = 300 mL, solvent = water, t = 40 min, T = 60 °C	[106]

Table 4
Applications of UAE in the extraction of compounds from oleaginous seeds.

Matrix	Extract	Processing device	Experimental conditions	Reference
Soybean, sunflower, rape	Oil	US probe/Soxhlet	m = 10 g, V = 100 mL, solvent = hexane, Irradiation time = 10 s (after the solvent reach the siphon height)	[76]
Almond	Oil	US bath (40 kHz, 150 W)	Solvent/sample ratio = 10–20(mg/L), solvent = hexane, t = 40–60 min, T = 40–60 °C	[75]
Papaya seed	Oil, antioxidants	US bath (40 kHz, 700 W)	P = 235–700 W, Sample/liquid ratio = 6/1–10/1 (V/w), solvent = hexane, t = 5–30 min, T = 25–50 °C,	[112,113]
Pistacia khinjuk kernel	Oil	US probe (30 kHz, 100 W, diameter = 10 mm)	Amplitude = 0, 25, 50%, pulse = 10 s on, 5 s off, ratio = 1/4 (w/V), solvent = hexane, T = 30, 40, 50 °C	[114]
Flaxseed	Oil	US probe (20 kHz, 250 W)	P = 50 W, ratio = 6/1 (V/w), solvent = hexane, V = 100 mL, t = 30 min, T = 30 °C	[73]
Soybean	Oil	US bath	I = 47.6 W/cm^2, solvent = hexane/isopropanol (3/2)	[63]

lipid extraction from microorganisms is a Bligh and Dyer modified procedure. A solution of EDTA (1 ml, 1 mM in 0.5 M acid acetic) was mixed to 10 mg of wet microalgae (20% dry weight). The mixture was transferred to a glass tube with 3 mL of chloroform: methanol (1:2, v/v), then covered with a screw cap in Teflon and vortexed (VX-2500, VWR). After, 1 mL of chloroform and 0.8 mL of KCl (0.88%, w/v) were added before being vortexed and centrifuged at 4000 rpm for 2 min. The lower chloroform phase was pipped and placed to a new glass tube. Cells were then extracted again with hexane, centrifuged and the supernatant was combined with the previous chloroform extracts. Finally lipid extracts were dried under a stream of N_2 and re-suspended in solvent for further analyses by GC–FID analysis. Ultrasound-assisted extraction was performed with success using a standard titanium sonotrode (area of 9 cm^2) combined to a booster and operating at 20 kHz with a 1000 W ultrasonic processor. For each experiment 100 g of wet *N. oculata* (30% dry weight) was submitted to sonication. An experimental design through response surface methodology (RSM) parameters was used and optimum conditions for oil extraction were estimated as follows: 1000 W ultrasonic power, 30 min extraction time and biomass dry weight content at 5 %. This study on non-starved microalgae has proved the efficiency of ultrasound for oil recovery in a reduced time and with a simple and scalable pre-industrial device. These conclusions were also supported by Piasecka et al. [121] for lipid extraction from *Chlorella protothecoides* microalgae. The ultrasonic pretreatment has improved the extraction yield of 42% and the palmitic acid content in the fatty acids profile. Other microorganisms such as oleaginous yeast *Trichosporon oleaginosisus* (ATCC20509) and oleaginous fungus (SkF-5) was also extracted by ultrasound in order to promote the lipid recovery [122]. In this case, ultrasonication of oleaginous microorganisms mixed with conventional solvent mixture (chloroform:methanol) allows to reduce extraction time from 12 hours to 15 min in comparison with the conventional method, without affecting fatty acids profile of the biofuel.

Ultrasound-assisted green solvent extraction is also a promising tool for recovering of other high-value compounds such as phenolic compounds and chlorophylls from microorganisms such as *Nannochloropsis* spp. microalgae [123]. The extraction yield of these high-value compounds was two times higher by UAE in comparison with conventional water extraction by maceration. Optimum operating conditions in order to obtain the maximum yield was 400 W, 5 min of sonication, and a binary mixture of solvents such as water:DMSO and water:EtOH.

Natural colors are very demanded by food and cosmetic industries as additives. Macias-Sanchez et al. [124] have proposed a comparative study of two innovative techniques: UAE and supercritical fluid for extraction of carotenoids and chlorophyll from *Dunaliella salina.* The study indicates that the supercritical fluid extraction process is comparable to the ultrasound-assisted extraction when methanol is used as solvent. In the case of UAE, the solvent N, N-dimethylformamide, DMF (more selective than methanol) gave higher yields for carotenoids and chlorophylls as well as for carotenoids/chlorophylls ratio. Another study based on a comparative study of carotenoids and fatty acids extracted from *Synechococcus* sp. with supercritical fluid and UAE using DMF. UAE allows higher concentrations of β-carotene than supercritical fluid, although the recovery of astaxanthin with ultrasound is low compared to SFE [125]. Table 5 presents applications of UAE for obtention of high value compounds from various microorganisms.

6. HACCP and HAZOP considerations using UAE

HACCP (Hazard Analysis and Critical Control Points) concept is a systematic approach to food safety management based on 7 recognized principles designed to identify and prevent the hazards likely to occur at any stage in the food supply chain [128]. A critical control point (CCP) is a step in the flow diagram of the food process at which control measures can be applied. These CCPs are essential to prevent or eliminate a food safety hazard or reduce it to an acceptable level.

Ultrasound is nowadays commonly used in many unit operations during food processing considering their physical effects for extraction, degassing or cutting, but also considering their chemical and biological effects for the inactivation of enzymes or the sterilization of equipment for example. However, the use of US in food engineering requires the setting-up of an HACCP program in which the CCPs are identified, so that potential hazards in producing a safe quality product can be controlled. These can be biological, chemical or physical hazards that need verification activities. Examples are given in Table 6. In the ultrasound treatment, the critical processing factors are assumed to be the amplitude of the ultrasonic wave, the time of exposure/contact with the microorganisms, the type of microorganism, the volume of food to be processed, the composition of the food, and the temperature of the treatment. During the development of the HACCP plan, the HACCP team must establish procedures to be followed if and when the monitoring of a CCP reveals that the critical limits are not respected, and therefore there is a loss of control of the hazard at the CCP. A product that is obtained during a processing step where the CCPs are not respected is described as non-conform and is likely to be unsafe if consumed.

Hazard and operability (HAZOP) study is a formal, systematic, logical, structured investigative study for examining potential deviations of operations from design conditions that could create process–operating problems and hazards [129]. It is one of the most structured techniques to identify hazards in a process plant and aims to find all possible deviations from the normal functioning of process parameters. HAZOP study analysis is the key critical tool used throughout processing industries worldwide. The technique was designed to optimize the process and improve performance. The purpose of the study is to provide a list of issues and recommendations for the prevention of each problem [129].

Table 5
Applications of UAE in the extraction of compounds from microorganisms.

Matrix	Extract	Processing device	Experimental conditions	Reference
Nannochloropsis oculata microalgae	Lipids	US probe (20 kHz, 1000 W, 9 cm^2)	t = 30 min biomass dry weight 5% solvent free	[120]
Trichosporon oleaginosisus yeast and oleaginous fungus (SkF-5)	Lipids	US horn (520 kHz, 40 W) US bath (50 Hz, 2800 W)	T = 25 °C t = 15 min Solvent: chloroform/methanol (1:2, v/v)	[122]
Nannochloropsis spp microalgae	Phenolic compounds and chlorophylls	US probe (24 kHz)	P = 100–400 W T < 60 °C t < 30 min m = 250 g suspended in Ethanol and DMSO	[123]
Dunaliella salina microalgae *Synechococcus* sp. cyanobacteria	Carotenoids and chlorophyll	US bath	t = 3 min m = 0.105 g of lyophilized microalgae in 5 mL DMF and methanol	[124,125]
Xanthophyllomyces dendrorhous yeast	Carotenoids (astaxanthin)	US bath	T = 40–60 °C t = 15–35 min 0.2 g lyophilized biomass in 10 mL of 5 mol/L lactic acid.	[126]
Cordycepssinensis fungus	Water-soluble components and polysaccharides	US probe (20 kHz)	UI = 2.44–44.1 W/cm^2 T = 40–70 °C, particle size = 156.5–750 µm solid/liquid ratio = 1/30–1/70 g/mL	[127]

Table 6
Examples of verification activities for CCPs.

Danger types	Verification activities
CCPs for Biological Hazards	
Sterilization	Review of pasteurization, records, microbiological testing of product periodically
Acidification	Review of pH measurement records, microbiological testing of product periodically
CCPs for Chemical Hazards	
Receiving of raw material	Review of certificates of analysis, periodic sampling and testing of raw material
Labeling	Review of labeling inspection records
CCPs for Physical Hazards	
Filtering	Review of filter inspection records
Metal detection	Review of metal detector records

The main hazard the users may face is from accidental contact exposure to the ultrasonic waves. Direct contact exposure can cause tissue injury for the operator. Moreover, ultrasound equipment are electrical devices that may present danger to operators. Electricity can cause electrical shock and burns, and be a potential fire hazard. Ultrasound can also generate indirect effects on the operator: (i) airborne ultrasound: it can affect the central nervous system and imply damages to the ear, (ii) heat and cavitation: it can cause burns and chronic lengthy exposures could raise body temperatures to mild fever levels during the exposure periods.

7. Environmental impact of Ultrasound-assisted extraction (UAE)

UAE is a clean method that avoids the use of large quantity of solvent and voluminous extraction vessels like Soxhlet and maceration. The reduced environmental impact of UAE is clearly advantageous in terms of energy and time. As an example, extraction of fat and oil from oleaginous seeds is performed with Soxhlet procedure, which needs to extract 50 g of seeds with 300 mL of hexane as solvent for 8 hours. The energy required to perform the three extraction methods are respectively 6 kW.h for maceration at the solvent's boiling point (electrical energy for mechanical mixing and for heating), 8 kW.h for Soxhlet (electrical energy for heating), and 0.25 kW.h for UAE (electrical energy for ultrasound supply). The power consumption was determined with a Wattmeter at the ultrasound generator supply and the electrical heater power supply. Regarding environmental impact, the calculated quantity of carbon dioxide rejected in the atmosphere is higher in the case of Soxhlet (6400 g CO_2/100 g of extracted solid material) and maceration (3600 g CO_2/100 g of extracted solid material) than for UAE (200 g CO_2/100 g of extracted solid material). These calculations have been carried out based on the following assumptions: to obtain 1 kW.h from coal or fuel, 800 g of CO_2 will be rejected in the atmosphere during combustion of fossil fuel. UAE is thus proposed as an "environmentally friendly" extraction method suitable for extraction at laboratory scale but could be also transposed to pilot and industrial scale.

8. Up-scaling of UAE and its applications in industry

To ensure safety, sustainability, economic and greener methods, the design of an efficient ultrasound-assisted large-scale extraction requires process intensification and energy consumption reduction. Both types of devices for high power ultrasound such as probe and bath systems are widely used industrially, due to their difference of potential and efficiency, the choice of the system will depend of the matrix and the application desired. Hielscher (Germany) and REUS (France) are the main companies which develop large-scale ultrasound extraction devices. The major parameter for an industrial setup is the quantity of product to be treated, ultrasonic probe are restricted for the small volume. One solution is the use of a continuous system that can handle a larger amount with a restrictive volume of reactor, ultrasound are then more concentrated with a maximum power per volume. Hielscher Company commercializes devices of a wide range power from 50 to 400 W for analytical scales and from 500 to 16,000 W in industrial scales (Fig. 11). The other alternative is to use ultrasonic baths with a larger radiating surface and an agitation system. REUS Company has developed a wide range of reactors from pilot (30 to 50 L), and industrial scale (500 to 1000 L), coupled with pump systems in order to fill the ultrasonic bath, to stir the mixture and to empty the system at the end of the procedure (Fig. 12).

Fig. 11. Industrial ultrasonic continuous equipments (Hielscher – www.hielscher.com).

Fig. 12. Industrial ultrasonic batch equipments: 50, 500 and 1000 L (Reus – www.etsreus.com).

An increasing number of companies already use the ultrasonic technology, either by adapting their conventional or innovative system of extraction or by changing their installation. In industrial scale, the majority of extracted compounds is directly used, as in liquor production or can be used as food and cosmetic additives, in the case of essential oil and bioactive molecules. Euphytos is an Italian company specialized in natural extracts from herbs, fruits and vegetables using ultrasound technology to improve the flavor and quality of the extracts. GMC (G. Mariani & C. Spa) company has also adapted their conventional extraction system in order to intensify aromatic herbs extracts. Giotti (Italian company) is equipped by four continuous batch systems coupled with ultrasound on each side of the tank and an agitation system. For this company, ultrasound is an effective assistance for food extraction, pharmaceutical additives, and production of alcoholic drinks.

9. Future trends

One of the great success stories of innovative extraction techniques has been the evolution of ultrasound extraction systems that directly translate knowledge into technology and commercial products. Utilization of ultrasound technology for extraction of food and natural extracts is such a system that has evolved to keep the wheel of development rolling. Ultrasound-assisted extraction makes use of physical and chemical phenomena that are fundamentally different compared with those applied in conventional extraction techniques. Ultrasound extraction process can produce green extracts in concentrate form, free from any residual solvents, contaminants, or artefacts. The new ultrasound systems developed to date offer net advantages in term of yield and selectivity, with better extraction time, extract quality and safety, easily integrated in industry, and are environmentally friendly.

Nowadays, the choice of which technique has to be used to perform extraction of a desired metabolite from a specific plant has to be a result of a compromise between the efficiency and reproducibility of extraction, ease of procedure, together with considerations of cost, time, safety and degree of automation. In this review we have discussed how the concept of ultrasound-assisted extraction has already become an important issue in the chemistry of natural products. Detailed analysis of past and present literature confirms explicitly the usefulness of this extraction method at laboratory and industrial scale. We have hope that this review will widen the scope of laboratory and commercial success for the potential applications of ultrasound technology in extraction of food and natural products.

References

[1] F. Chemat, N. Rombaut, A.-S. Fabiano-Tixier, J.T. Pierson, A. Bily, Chapter 1. Green extraction: from concepts to research, education, and economical opportunities, in: F. Chemat, J. Strube (Eds.), Green Extraction of Natural Products: Theory and Practice, Wiley CH, 2015, pp. 1–36.
[2] F. Chemat, M.A. Vian, G. Cravotto, Green extraction of natural products: concept and principles, Int. J. Mol. Sci. 13 (2012) 8615–8627.
[3] N. Rombaut, A.-S. Tixier, A. Bily, F. Chemat, Green extraction processes of natural products as tools for biorefinery, Biofuels, Bioprod. Biorefin. 8 (2014) 530–544.
[4] G. Cravotto, P. Cintas, Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications, Chem. Soc. Rev. 35 (2006) 180–196.
[5] M. Vinatoru, Ultrasonically assisted extraction (UAE) of natural products some guidelines for good practice and reporting, Ultrason. Sonochem. 25 (2015) 94–95.
[6] F. Chemat, Zill-e-Huma, M. Kamran Khan, Applications of ultrasound in food technology: processing, preservation and extraction, Ultrason. Sonochem. 18 (2011) 813–835.
[7] S.R. Shirsath, S.H. Sonawane, P.R. Gogate, Intensification of extraction of natural products using ultrasonic irradiations—a review of current status, Chem. Eng. Proc. 53 (2012) 10–23.
[8] B.K. Tiwari, Ultrasound: a clean, green extraction technology, TrAC Trends Anal. Chem. 71 (2015) 100–109.
[9] K. Vilkhu, R. Mawson, L. Simons, D. Bates, Applications and opportunities for ultrasound assisted extraction in the food industry — a review, Innov. Food Sci. Emerg. Technol. 9 (2008) 161–169.
[10] T.J. Mason, J.P. Lorimer, General principles, in: T.J. Mason, J.P. Lorimer (Eds.), Applied Sonochemistry: Uses of Power Ultrasound in Chemistry and Processing, Wiley-VCH Verlag, Germany, 2002, pp. 25–74.
[11] K.S. Suslick, G.J. Price, Applications of ultrasound to materials chemistry, Ann. Rev. Mater. Sci. 29 (1999) 295–326.
[12] M. Toma, M. Vinatoru, L. Paniwnyk, T.J. Mason, Investigation of the effects of ultrasound on vegetal tissues during solvent extraction, Ultrason. Sonochem. 8 (2001) 137–142.
[13] K.A. Kusters, S.E. Pratsinis, S.G. Thoma, D.M. Smith, Ultrasonic fragmentation of agglomerate powders, Chem. Eng. Sci. 48 (1993) 4119–4127.
[14] K.A. Kusters, S.E. Pratsinis, S.G. Thoma, D.M. Smith, Energy—size reduction laws for ultrasonic fragmentation, Powder Technol. 80 (1994) 253–263.
[15] L. Petigny, S. Périno-Issartier, J. Wajsman, F. Chemat, Batch and continuous ultrasound assisted extraction of boldo leaves (*Peumus boldus* Mol.), Int. J. Mol. Sci. 14 (2013) 5750–5764.
[16] K.S. Suslick, M.M. Fang, T. Hyeon, M.M. Mdleleni, Applications of sonochemistry to materials synthesis, in: L.A. Crum, T.J. Mason, J.L. Reisse, K.S. Suslick (Eds.), Sonochemistry and Sonoluminescence, Springer, USA, 1999, pp. 291–320.
[17] M. Degrois, D. Gallant, P. Baldo, A. Guilbot, The effects of ultrasound on starch grains, Ultrasonics 12 (1974) 129–131.
[18] T.J. Mason, Some neglected or rejected paths in sonochemistry – a very personal view, Ultrason. Sonochem. 25 (2015) 89–93.
[19] N. Malykh, V. Petrov, G. Sankin, On sonocapillary effect, in: Proceedings of the 5th World Congress on Ultrasonics (WCU). Paris, 2003, pp. 1343–1346.
[20] I. Tzanakis, W.W. Xu, D.G. Eskin, P.D. Lee, N. Kotsovinos, *In situ* observation and analysis of ultrasonic capillary effect in molten aluminium, Ultrason. Sonochem. 27 (2015) 72–80.
[21] N.V. Dezhkunov, T.G. Leighton, Study into correlation between the ultrasonic capillary effect and sonoluminescence, J. Eng. Phys. Thermophys. 77 (2004) 53–61.
[22] D. Pingret, A.-S. Fabiano-Tixier, C.L. Bourvellec, C.M.G.C. Renard, F. Chemat, Lab and pilot-scale ultrasound-assisted water extraction of polyphenols from apple pomace, J. Food Eng. 111 (2012) 73–81.
[23] Y.-L. Huang, Y.-S. Ma, The effect of extrusion processing on the physiochemical properties of extruded orange pomace, Food Chem. 192 (2016) 363–369.
[24] M. Vinatoru, An overview of the ultrasonically assisted extraction of bioactive principles from herbs, Ultrason. Sonochem. 8 (2001) 303–313.
[25] I. Siró, C. Vén, C. Balla, G. Jónás, I. Zeke, L. Friedrich, Application of an ultrasonic assisted curing technique for improving the diffusion of sodium chloride in porcine meat, J. Food Eng. 91 (2009) 353–362.
[26] J. Stadnik, Z.J. Dolatowski, H.M. Baranowska, Effect of ultrasound treatment on water holding properties and microstructure of beef (m. semimembranosus) during ageing, LWT – Food Science and Technology 41 (2008) 2151–2158.
[27] J.A. Cárcel, J. Benedito, J. Bon, A. Mulet, High intensity ultrasound effects on meat brining, Meat Sci. 76 (2007) 611–619.
[28] C. Ozuna, A. Puig, J.V. García-Pérez, A. Mulet, J.A. Cárcel, Influence of high intensity ultrasound application on mass transport, microstructure and textural properties of pork meat (Longissimus dorsi) brined at different NaCl concentrations, J. Food Eng. 119 (2013) 84–93.
[29] C.K. McDonnell, P. Allen, C. Morin, J.G. Lyng, The effect of ultrasonic salting on protein and water–protein interactions in meat, Food Chem. 147 (2014) 245–251.
[30] R. Karshafian, P.D. Bevan, R. Williams, S. Samac, P.N. Burns, Sonoporation by ultrasound-activated microbubble contrast agents: effect of acoustic exposure parameters on cell membrane permeability and cell viability, Ultrasound Med. Biol. 35 (2009) 847–860.
[31] S. Ohta, K. Suzuki, S. Miyagawa, Y. Ogino, M. Villacorte, Y. Wada, G. Yamada, Chapter 27: Sonoporation in developmental biology, in: H. Nakamura (Ed.), Electroporation and Sonoporation in Developmental Biology, Springer, Japan, 2009, pp. 317–326.
[32] D.L. Miller, S.V. Pislaru, J.E. Greenleaf, Sonoporation: mechanical DNA delivery by ultrasonic cavitation, Somat. Cell. Mol. Genet. 27 (2002) 115–134.
[33] E. Ugarte-Romero, H. Feng, S.E. Martin, K.R. Cadwallader, S.J. Robinson, Inactivation of *Escherichia coli* with power ultrasound in apple cider, J. Food Sci. 71 (2006) E102–E108.
[34] A. Meullemiestre, C. Breil, M. Abert-Vian, F. Chemat, Microwave, ultrasound, thermal treatments, and bead milling as intensification techniques for extraction of lipids from oleaginous Yarrowia lipolytica yeast for a biojetfuel application, Bioresour. Technol. 211 (2016) 190–199.
[35] K. Vilkhu, R. Manasseh, R. Mawson, M. Ashokkumar, Ultrasonic recovery and modification of food ingredients, in: H. Feng, G. Barbosa-Canovas, J. Weiss (Eds.), Ultrasound Technologies for Food and Bioprocessing, Springer, New York, USA, 2011, pp. 345–368.
[36] S. Veillet, V. Tomao, F. Chemat, Ultrasound assisted maceration: an original procedure for direct aromatisation of olive oil with basil, Food Chem. 123 (2010) 905–911.
[37] D.R. Gang, J. Wang, N. Dudareva, K.H. Nam, J.E. Simon, E. Lewinsohn, E. Pichersky, An investigation of the storage and biosynthesis of phenylpropenes in sweet basil, Plant Physiol. 125 (2001) 539–555.
[38] M. Vinatoru, M. Toma, O. Radu, P.I. Filip, D. Lazurca, T.J. Mason, The use of ultrasound for the extraction of bioactive principles from plant materials, Ultrason. Sonochem. 4 (1997) 135–139.
[39] S. Chemat, A. Lagha, H. AitAmar, P.V. Bartels, F. Chemat, Comparison of conventional and ultrasound-assisted extraction of carvone and limonene from caraway seeds, Flavour Frag. J. 19 (2004) 188–195.
[40] T.J. Mason, L. Paniwnyk, J.P. Lorimer, The uses of ultrasound in food technology, Ultrason. Sonochem. 3 (1996) S253–S260.
[41] S. Kentish, M. Ashokkumar, The physical and chemical effects of ultrasound, in: H. Feng, G. Barbosa-Canovas, J. Weiss (Eds.), Ultrasound Technologies for Food and Bioprocessing, Springer, USA, 2011, pp. 1–12.
[42] K.S. Suslick, The chemical effects of ultrasound, Sci. Am. 260 (1989) 80–86.
[43] M. Ashokkumar, The characterization of acoustic cavitation bubbles – an overview, Ultrason. Sonochem. 18 (2011) 864–872.
[44] T. Leong, M. Ashokkumar, S. Kentish, The fundamentals of power ultrasound: a review, Acoust. Aust. 39 (2011) 54–63.

[45] E.B. Flint, K.S. Suslick, The temperature of cavitation, Science 253 (1991) 1397–1399.
[46] K.S. Suslick, Y. Didenko, M.M. Fang, T. Hyeon, K.J. Kolbeck, W.B. McNamara, M.M. Mdleleni, M. Wong, Acoustic cavitation and its chemical consequences, Philos. Trans. R. Soc. London, Ser. A 357 (1999) 335–353.
[47] D. Pingret, A.-S. Fabiano-Tixier, F. Chemat, Chapter 3: Ultrasound-assisted extraction, in: M.A. Rostagno, J.M. Prado (Eds.), Natural Product Extraction: Principles and Applications, The Royal Society of Chemistry, UK, 2013, pp. 89–112.
[48] M.M. Chivate, A.B. Pandit, Quantification of cavitation intensity in fluid bulk, Ultrason. Sonochem. 2 (1995) S19–S25.
[49] M.A. Margulis, I.M. Margulis, Calorimetric method for measurement of acoustic power absorbed in a volume of a liquid, Ultrason. Sonochem. 10 (2003) 343–345.
[50] C.J. Martin, A.N.R. Law, Design of thermistor probes for measurement of ultrasound intensity distributions, Ultrasonics 21 (1983) 85–90.
[51] K. Makino, M.M. Mossoba, P. Riesz, Chemical effects of ultrasound on aqueous solutions. Formation of hydroxyl radicals and hydrogen atoms, J. Phys. Chem. 87 (1983) 1369–1377.
[52] K.S. Suslick, N.C. Eddingsaas, D.J. Flannigan, S.D. Hopkins, H. Xu, Extreme conditions during multibubble cavitation: sonoluminescence as a spectroscopic probe, Ultrason. Sonochem. 18 (2011) 842–846.
[53] R.F. Contamine, A.M. Wilhelm, J. Berlan, H. Delmas, Power measurement in sonochemistry, Ultrason. Sonochem. 2 (1995) S43–S47.
[54] M. Toma, S. Fukutomi, Y. Asakura, S. Koda, A calorimetric study of energy conversion efficiency of a sonochemical reactor at 500 kHz for organic solvents, Ultrason. Sonochem. 18 (2011) 197–208.
[55] D. Bermúdez-Aguirre, T. Mobbs, G. Barbosa-Cánovas, Ultrasound applications in food processing, in: H. Feng, G. Barbosa-Canovas, J. Weiss (Eds.), Ultrasound Technologies for Food and Bioprocessing, Springer, New York, USA, 2011, pp. 65–105.
[56] X. Wei, M. Chen, J. Xiao, Y. Liu, L. Yu, H. Zhang, Y. Wang, Composition and bioactivity of tea flower polysaccharides obtained by different methods, Carbohydr. Polym. 79 (2010) 418–422.
[57] C. Pétrier, N. Gondrexon, P. Boldo, Ultrasons et sonochimie, Techniques de l'ingénieur Chimie verte: optimisation des modes de séparation, d'activation et de synthèse base documentaire: TIB493DUO, 2008.
[58] Y.C. Chukwumah, L.T. Walker, M. Verghese, S. Ogutu, Effect of frequency and duration of ultrasonication on the extraction efficiency of selected isoflavones and trans-resveratrol from peanuts (*Arachis hypogaea*), Ultrason. Sonochem. 16 (2009) 293–299.
[59] M.R. González-Centeno, K. Knoerzer, H. Sabarez, S. Simal, C. Rosselló, A. Femenia, Effect of acoustic frequency and power density on the aqueous ultrasonic-assisted extraction of grape pomace (*Vitis vinifera* L.) – a response surface approach, Ultrason. Sonochem. 21 (2014) 2176–2184.
[60] T.J. Mason, A.J. Cobley, J.E. Graves, D. Morgan, New evidence for the inverse dependence of mechanical and chemical effects on the frequency of ultrasound, Ultrason. Sonochem. 18 (2011) 226–230.
[61] M.D. Esclapez, J.V. García-Pérez, A. Mulet, J.A. Cárcel, Ultrasound-assisted extraction of natural products, Food Eng. Rev. 3 (2011) 108–120.
[62] H.M. Santos, C. Lodeiro, J.-L. Capelo-Martínez, The power of ultrasound, in: J.-L. Capelo-Martínez (Ed.), Ultrasound in Chemistry: Analytical Applications, Wiley-VCH Verlag, Germany, 2009, pp. 1–16.
[63] H. Li, L. Pordesimo, J. Weiss, High intensity ultrasound-assisted extraction of oil from soybeans, Food Res. Int. 37 (2004) 731–738.
[64] W. Wang, X. Ma, Y. Xu, Y. Cao, Z. Jiang, T. Ding, X. Ye, D. Liu, Ultrasound-assisted heating extraction of pectin from grapefruit peel: optimization and comparison with the conventional method, Food Chem. 178 (2015) 106–114.
[65] J.P. Lorimer, T.J. Mason, Sonochemistry. Part 1-The physical aspects, Chem. Soc. Rev. 16 (1987) 239–274.
[66] Y. Sun, D. Liu, J. Chen, X. Ye, D. Yu, Effects of different factors of ultrasound treatment on the extraction yield of the all-trans-β-carotene from citrus peels, Ultrason. Sonochem. 18 (2011) 243–249.
[67] M.D. Esclapez, V. Sáez, D. Milán-Yáñez, I. Tudela, O. Louisnard, J. González-García, Sonoelectrochemical treatment of water polluted with trichloroacetic acid: from sonovoltammetry to pre-pilot plant scale, Ultrason. Sonochem. 17 (2010) 1010–1020.
[68] G. Cravotto, L. Boffa, S. Mantegna, P. Perego, M. Avogadro, P. Cintas, Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves, Ultrason. Sonochem. 15 (2008) 898–902.
[69] D.J. Flannigan, K.S. Suslick, Inertially confined plasma in an imploding bubble, Nat. Phys. 6 (2010) 598–601.
[70] M. Sališová, Š. Toma, T.J. Mason, Comparison of conventional and ultrasonically assisted extractions of pharmaceutically active compounds from *Salvia officinalis*, Ultrason. Sonochem. 4 (1997) 131–134.
[71] M. Palma, G.F. Barbero, Z. Pineiro, A. Liazid, C.G. Barroso, M.A. Rostagno, J.M. Prado, M.A.A. Meireles, Chapter 2: Extraction of natural products: principles and fundamental aspects, in: M.A. Rostagno, J.M. Prado (Eds.), Natural Product Extraction: Principles and Applications, The Royal Society of Chemistry, UK, 2013, pp. 58–88.
[72] M. Palma, C.G. Barroso, Ultrasound-assisted extraction and determination of tartaric and malic acids from grapes and winemaking by-products, Anal. Chim. Acta 458 (2002) 119–130.
[73] Z.-S. Zhang, L.-J. Wang, D. Li, S.-S. Jiao, X.D. Chen, Z.-H. Mao, Ultrasound-assisted extraction of oil from flaxseed, Sep. Purif. Technol. 62 (2008) 192–198.
[74] H.-F. Zhang, X.-H. Yang, L.-D. Zhao, Y. Wang, Ultrasonic-assisted extraction of epimedin C from fresh leaves of Epimedium and extraction mechanism, Innov. Food Sci. Emerg. Technol. 10 (2009) 54–60.
[75] Q.-A. Zhang, Z.-Q. Zhang, X.-F. Yue, X.-H. Fan, T. Li, S.-F. Chen, Response surface optimization of ultrasound-assisted oil extraction from autoclaved almond powder, Food Chem. 116 (2009) 513–518.
[76] J.L. Luque-García, M.D. Luque de Castro, Ultrasound-assisted soxhlet extraction: an expeditive approach for solid sample treatment: application to the extraction of total fat from oleaginous seeds, J. Chromatogr. A 1034 (2004) 237–242.
[77] Z. Djenni, D. Pingret, T.J. Mason, F. Chemat, Sono–Soxhlet: *in situ* ultrasound-assisted extraction of food products, Food Anal. Met. 6 (2012) 1229–1233.
[78] D. Pingret, A.-S. Fabiano-Tixier, F. Chemat, An improved ultrasound clevenger for extraction of essential oils, Food Anal. Met. 7 (2013) 9–12.
[79] G. Cravotto, P. Cintas, The combined use of microwaves and ultrasound: improved tools in process chemistry and organic synthesis, Chemistry 13 (2007) 1902–1909.
[80] G. Cravotto, A. Binello, Innovative techniques and equipments for flavours extraction. Application and effectiveness of ultrasound and microwaves, Household Pers. Care Today 1 (2010) 32–34.
[81] T. Allaf, V. Tomao, K. Ruiz, F. Chemat, Instant controlled pressure drop technology and ultrasound assisted extraction for sequential extraction of essential oil and antioxidants, Ultrason. Sonochem. 20 (2013) 239–246.
[82] S. Balachandran, S.E. Kentish, R. Mawson, M. Ashokkumar, Ultrasonic enhancement of the supercritical extraction from ginger, Ultrason. Sonochem. 13 (2006) 471–479.
[83] J. Chen, Y. Chen, H. Li, S.-Y. Lai, J. Jow, Physical and chemical effects of ultrasound vibration on polymer melt in extrusion, Ultrason. Sonochem. 17 (2010) 66–71.
[84] S.A.A.A. Mousavi, H. Feizi, R. Madoliat, Investigations on the effects of ultrasonic vibrations in the extrusion process, J. Mater. Proc. Technol. 187–188 (2007) 657–661.
[85] R.A.A. Mothana, Anti-inflammatory, antinociceptive and antioxidant activities of the endemic Soqotraen *Boswellia elongata* Balf. f. and *Jatropha unicostata* Balf. f. in different experimental models, Food Chem. Toxicol. 49 (2011) 2594–2599.
[86] C. Sarikurkcu, B. Tepe, D. Daferera, M. Polissiou, M. Harmandar, Studies on the antioxidant activity of the essential oil and methanol extract of *Marrubium globosum* subsp. *globosum* (lamiaceae) by three different chemical assays, Biores. Technol. 99 (2008) 4239–4246.
[87] C.Y. Wang, B.H. Chen, Tomato pulp as source for the production of lycopene powder containing high proportion of cis-isomers, Eur. Food Res. Technol. 222 (2006) 347–353.
[88] Z. Pan, W. Qu, H. Ma, G.G. Atungulu, T.H. McHugh, Continuous and pulsed ultrasound-assisted extractions of antioxidants from pomegranate peel, Ultrason. Sonochem. 19 (2012) 365–372.
[89] K.M. Hammi, A. Jdey, C. Abdelly, H. Majdoub, R. Ksouri, Optimization of ultrasound-assisted extraction of antioxidant compounds from Tunisian *Zizyphus lotus* fruits using response surface methodology, Food Chem. 184 (2015) 80–89.
[90] E. Luengo, S. Condón-Abanto, S. Condón, I. Álvarez, J. Raso, Improving the extraction of carotenoids from tomato waste by application of ultrasound under pressure, Sep. Purif. Technol. 136 (2014) 130–136.
[91] V. Sivakumar, J. Vijaeeswarri, J.L. Anna, Effective natural dye extraction from different plant materials using ultrasound, Ind. Crops Prod. 33 (2011) 116–122.
[92] A.C. Kimbaris, N.G. Siatis, D.J. Daferera, P.A. Tarantilis, C.S. Pappas, M.G. Polissiou, Comparison of distillation and ultrasound-assisted extraction methods for the isolation of sensitive aroma compounds from garlic (*Allium sativum*), Ultrason. Sonochem. 13 (2006) 54–60.
[93] S. Rodrigues, F.A.N. Fernandes, E.S. de Brito, A.D. Sousa, N. Narain, Ultrasound extraction of phenolics and anthocyanins from jabuticaba peel, Ind. Crops Prod. 69 (2015) 400–407.
[94] K. Ghafoor, Y.H. Choi, J.Y. Jeon, I.H. Jo, Optimization of ultrasound-assisted extraction of phenolic compounds, antioxidants, and anthocyanins from grape (*Vitis vinifera*) seeds, J. Agric. Food Chem. 57 (2009) 4988–4994.
[95] Pharmacopée Européene 8.0, Huiles essentielles – Aetherolea (01/2008:2098), 2008.
[96] F. Chemat, G. Cravotto, Chapter 6: Combined extraction techniques, in: N. Lebovka, E. Vorobiev, F. Chemat (Eds.), Enhancing Extraction Processes in the Food Industry, CRC Press, Cambridge, 2011, pp. 173–193.
[97] C. Da Porto, D. Decorti, Ultrasound-assisted extraction coupled with under vacuum distillation of flavour compounds from spearmint (carvone-rich) plants: comparison with conventional hydrodistillation, Ultrason. Sonochem. 16 (2009) 795–799.
[98] K. Assami, D. Pingret, S. Chemat, B.Y. Meklati, F. Chemat, Ultrasound induced intensification and selective extraction of essential oil from *Carum carvi* L. seeds, Chem. Eng. Process. 62 (2012) 99–105.
[99] G.F. Barbero, A. Liazid, M. Palma, C.G. Barroso, Ultrasound-assisted extraction of capsaicinoids from peppers, Talanta 75 (2008) 1332–1337.
[100] S. Boonkird, C. Phisalaphong, M. Phisalaphong, Ultrasound-assisted extraction of capsaicinoids from *Capsicum frutescens* on a lab- and pilot-plant scale, Ultrason. Sonochem. 15 (2008) 1075–1079.
[101] S. Albu, E. Joyce, L. Paniwnyk, J.P. Lorimer, T.J. Mason, Potential for the use of ultrasound in the extraction of antioxidants from *Rosmarinus officinalis* for

the food and pharmaceutical industry, Ultrason. Sonochem. 11 (2004) 261–265.
[102] L. Paniwnyk, H. Cai, S. Albu, T.J. Mason, R. Cole, The enhancement and scale up of the extraction of anti-oxidants from *Rosmarinus officinalis* using ultrasound, Ultrason. Sonochem. 16 (2009) 287–292.
[103] M. Jacotet-Navarro, N. Rombaut, A.S. Fabiano-Tixier, M. Danguien, A. Bily, F. Chemat, Ultrasound versus microwave as green processes for extraction of rosmarinic, carnosic and ursolic acids from rosemary, Ultrason. Sonochem. 27 (2015) 102–109.
[104] M.B. Hossain, N.P. Brunton, A. Patras, B. Tiwari, C.P. O'Donnell, A.B. Martin-Diana, C. Barry-Ryan, Optimization of ultrasound assisted extraction of antioxidant compounds from marjoram (*Origanum majorana* L.) using response surface methodology, Ultrason. Sonochem. 19 (2012) 582–590.
[105] H. Sereshti, R. Heidari, S. Samadi, Determination of volatile components of saffron by optimised ultrasound-assisted extraction in tandem with dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry, Food Chem. 143 (2014) 499–505.
[106] T. Xia, S. Shi, X. Wan, Impact of ultrasonic-assisted extraction on the chemical and sensory quality of tea infusion, J. Food Eng. 74 (2006) 557–560.
[107] Terres Inovia, Production de graines oélagineuses. http://www.terresinovia.fr/debouches-chiffres/les-cultures-en-chiffres/oleagineux/production/graines-oleagineuses/, 2013 (accessed 16.09.15).
[108] M.A.A. Meireles, Extracting Bioactive Compounds for Food Products: Theory and Applications, CRC Press, USA, 2008.
[109] P.J. Wan, P.J. Wakelyn, Technology and Solvents for Extracting Oilseeds and Nonpetroleum Oils, The American Oil Chemists Society, USA, 1997.
[110] F. Soxhlet, Die gewichtsanalytische bestimmung des Milchfettes, Dingler' Polytechnischen J. (1879) 461–465.
[111] Afnor, NF EN ISO 659 – Graines oléagineuses – Détermination de la teneur en huile (Méthode de référence). http://www.boutique.afnor.org/norme/nf-en-iso-659/graines-oleagineuses-determination-de-la-teneur-en-huile-methode-de-reference/article/750655/fa153459, 2009 (accessed 21.01.15).
[112] S. Samaram, H. Mirhosseini, C.P. Tan, H.M. Ghazali, Ultrasound-assisted extraction and solvent extraction of papaya seed oil: crystallization and thermal behavior, saturation degree, color and oxidative stability, Ind. Crops Prod. 52 (2014) 702–708.
[113] S. Samaram, H. Mirhosseini, C.P. Tan, H.M. Ghazali, S. Bordbar, A. Serjouie, Optimisation of ultrasound-assisted extraction of oil from papaya seed by response surface methodology: oil recovery, radical scavenging antioxidant activity, and oxidation stability, Food Chem. 172 (2015) 7–17.
[114] S.M.B. Hashemi, J. Michiels, S.H. Asadi Yousefabad, M. Hosseini, Kolkhoung (*Pistacia khinjuk*) kernel oil quality is affected by different parameters in pulsed ultrasound-assisted solvent extraction, Ind. Crops Prod. 70 (2015) 28–33.
[115] P. Dey, M.K. Maiti, Molecular characterization of a novel isolate of *Candida tropicalis* for enhanced lipid production, J. Appl. Microbiol. 114 (2013) 1357–1368.
[116] D. Gao, J. Zeng, Y. Zheng, X. Yu, S. Chen, Microbial lipid production from xylose by *Mortierella isabellina*, Biores. Technol. 133 (2013) 315–321.
[117] J.A. Aranda-Burgos, F. da Costa, S. Nóvoa, J. Ojea, D. Martínez-Patiño, Effects of microalgal diet on growth, survival, biochemical and fatty acid composition of *Ruditapes decussatus* larvae, Aquaculture 420–421 (2014) 38–48.
[118] E.G. Bligh, W.J. Dyer, A rapid method of total lipid extraction and purification, Can. J. Biochem. Physiol. 37 (1959) 911–917.
[119] J. Folch, M. Lees, G.H. Sloane Stanley, A simple method for the isolation and purification of total lipides from animal tissues, J. Biol. Chem. 226 (1957) 497–509.
[120] F. Adam, M. Abert-Vian, G. Peltier, F. Chemat, "Solvent-free" ultrasound-assisted extraction of lipids from fresh microalgae cells: a green, clean and scalable process, Biores. Technol. 114 (2012) 457–465.
[121] A. Piasecka, I. Krzemińska, J. Tys, Physical methods of microalgal biomass pretreatment, Int. Agrophys. 28 (2014) 341–348.
[122] X. Zhang, S. Yan, R.D. Tyagi, P. Drogui, R.Y. Surampalli, Ultrasonication assisted lipid extraction from oleaginous microorganisms, Biores. Technol. 158 (2014) 253–261.
[123] O. Parniakov, E. Apicella, M. Koubaa, F.J. Barba, N. Grimi, N. Lebovka, G. Pataro, G. Ferrari, E. Vorobiev, Ultrasound-assisted green solvent extraction of high-added value compounds from microalgae *Nannochloropsis* spp, Biores. Technol. 198 (2015) 262–267.
[124] M.D. Macías-Sánchez, C. Mantell, M. Rodríguez, E. Martínez de la Ossa, L.M. Lubián, O. Montero, Comparison of supercritical fluid and ultrasound-assisted extraction of carotenoids and chlorophyll a from *Dunaliella salina*, Talanta 77 (2009) 948–952.
[125] L.C. Cardoso, C.M. Serrano, M.R. Rodríguez, E.J.M. de la Ossa, L.M. Lubián, Extraction of carotenoids and fatty acids from microalgae using supercritical technology, Am. J. Anal. Chem. 3 (2012) 877–883.
[126] W. Wei, Y. Xin, Optimization of ultrasound-assisted extraction procedure to determine astaxanthin in *Xanthophyllomyces dendrorhous* by Box-Behnken design, Adv. J. Food Sci. Technol. 5 (2013) 1536–1542.
[127] Y.-C. Cheung, J.-Y. Wu, Kinetic models and process parameters for ultrasound-assisted extraction of water-soluble components and polysaccharides from a medicinal fungus, Biochem. Eng. J. 79 (2013) 214–220.
[128] F. Chemat, N. Hoarau, Hazard analysis and critical control point (HACCP) for an ultrasound food processing operation, Ultrason. Sonochem. 11 (2004) 257–260.
[129] N.L. Rossing, M. Lind, N. Jensen, S.B. Jørgensen, A functional HAZOP methodology, Comput. Chem. Eng. 34 (2010) 244–253.