Food Eng Rev (2016) 8:214–234
DOI 10.1007/s12393-015-9131-1

REVIEW ARTICLE

Application of Non-conventional Extraction Methods: Toward a Sustainable and Green Production of Valuable Compounds from Mushrooms

Elena Roselló-Soto[1] · Oleksii Parniakov[2,3] · Qian Deng[4] · Ankit Patras[5] · Mohamed Koubaa[2] · Nabil Grimi[2] · Nadia Boussetta[2] · Brijesh K. Tiwari[6] · Eugène Vorobiev[2] · Nikolai Lebovka[3] · Francisco J. Barba[1]

Received: 9 March 2015 / Accepted: 26 August 2015 / Published online: 9 September 2015

Abstract Mushrooms are a great source of nutritionally valuable compounds, including proteins, lipids, polysaccharides, polyphenols, micronutrients and vitamins. In particular, they are a significant dietary source of B group vitamins and can be an ideal vehicle in order to supply these vitamins for vegetarians. Conventional extraction methods usually involve water or organic solvents and may results in the noticeable degradation of components. This review describes the potential use of the novel non-conventional methods including enzyme-assisted extraction, pulsed electric fields, ultrasounds, microwaves, subcritical and supercritical fluid extraction for recovery of valuable compounds from mushrooms. Recent studies have shown the great potential of these environmentally friendly methods for green production of specific compounds for use as nutraceuticals or as ingredients for functional foods.

Keywords Mushrooms · Nutritional compounds · Assisted extraction · Enzyme-assisted extraction · Pulsed electric technologies · Acoustic technologies · Subcritical and supercritical fluid extraction

✉ Francisco J. Barba
francisco.barba@uv.es

[1] Nutrition and Food Science Area, Faculty of Pharmacy, Universitat de València, Avda. Vicent Andrés Estellés, s/n, 46100 Burjassot, València, Spain

[2] Laboratoire Transformations Intégrées de la Matière Renouvelable (UTC/ESCOM, EA 4297 TIMR), Centre de Recherche de Royallieu, Sorbonne Universités, Université de Technologie de Compiègne, B.P. 20529, 60205 Compiègne Cedex, France

[3] Institute of Biocolloidal Chemistry (named after F.D. Ovcharenko), NAS of Ukraine, 42, blvr. Vernadskogo, Kiev 03142, Ukraine

[4] Wm. Bolthouse Farms, Inc., 7200 East Brundage Ln, Bakersfield, CA 93307, USA

[5] Department of Agricultural and Environmental Sciences, College of Agriculture, Human and Natural Sciences, Tennessee State University, 3500 John A Merritt Blvd, Nashville, TN 37209, USA

[6] Department of Food Biosciences, Teagasc Food Research Centre, Ashtown, Dublin 15, Ireland

Introduction

Mushrooms have been part of human diet for thousands of years, and recently their consumption is increasing around the world [1, 2]. Over the last years, they have been used as source of food additives for human nutrition, nutraceuticals, and nutritional supplements as they are a good source of valuable compounds with high nutritional properties. Most of these bioactive compounds have demonstrated the potential for the treatment and prevention of human diseases, mainly attributed to their antioxidant properties [3]. They can efficiently interact with proteins, DNA, and other biological molecules to produce a desired outcome, which could be exploited for designing natural products-derived therapeutic agents [4].

One of the main problems to obtain nutritionally valuable compounds from mushrooms in energy-efficiently and economically sustainable way is the difficulty to release them from their complex matrix and intracellular location, avoiding the use of large amounts of solvent and long extraction time. Conventional methods usually involve water or organic solvent for extraction depending on the target compound and their end use. However, these techniques are time consuming and may result in the degradation and coagulation of valuable compounds that can be

found in mushrooms. Moreover, organic solvent extraction involves the use of high cost solvents (i.e., ethanol). To avoid these limitations, the different non-conventional methods of extraction assisted by enzymes, pulsed electric fields (PEF), ultrasound, microwaves, and using of sub-critical and supercritical fluids were recently developed.

This review focused on the present developments in application of the modern non-conventional techniques to recover nutritionally valuable compounds from mushrooms.

Mushroom Structure and Nutritional Profile

There are about 10,000 known types of mushrooms around the world. They can be divided in different categories and the most commonly used are the edible mushrooms. The edible mushrooms have no poisonous effects, display the desirable taste and aroma and have rich content of valuable compounds. The short information about the most commonly used edible mushrooms is presented in Table 1.

Different mushrooms can provide a significant content of nutritionally valuable compounds including proteins, lipids, polysaccharides, microelement vitamins, and some important bioactive compounds (i.e., polyphenols) [5–7]. Figure 1 shows an example of a typical fungal cell and the location of some important compounds inside it. The structure of a fungal cell is similar to the structure of a plant cell. However, a fungal cell wall contains no chloroplasts inside the cell.

Table 2 presents macronutrients (proteins, carbohydrates, lipids) and amino acid profile (fresh weight basis) of some mushroom species [8, 9].

The content of macronutrients is ≈1.8–7.4 g/100 g for proteins, ≈4.5–6.3 g/100 g for carbohydrates and ≈0.2–1.7 g/100 g for lipids. The contents of the overall fatty acids and vitamins found in mushroom species are presented in Table 3 [10–13] and Table 4 [5, 7, 14–19], respectively.

Table 1 Information about the most commonly used edible mushrooms

Scientific name (species)	Photo	English name
Agaricus bisporus		White, brown mushroom
Amanita caesarea		Caesar's mushroom
Boletus edulis		Penny bun
Cantharellus cibarius		Chanterelle, golden chanterelle or girolle
Cantharellus lutescens		Yellow foot
Craterellus cornucopioides		Trumpet of the dead, black chanterelle, poor man's truffle, black trumpet, or horn of plenty
Hydnum repandum		Wood Hedgehog or Hedgehog mushroom
Lactarius deliciosus		Saffron milk cap, red pine mushroom
Lentinula edodes		Shiitake
Lepista nuda		Wood blewit or blue stalk mushroom
Pleurotus eryngii		King brown mushroom
Pleurotus ostreatus		Oyster mushroom
Russula cyanoxantha		Charcoal burner

Techniques of Extraction

Short Information on Conventional Methods

Traditionally, solvent-assisted extraction of valuable components has been used to recover valuable compounds from mushrooms [20, 21]. For instance, water extraction is a widely employed technique as it is an economic method, and does not requires any special equipment. However, water extraction requires high temperatures (T = 50–80 °C) [22, 23] and long treatment times (t = 1.5–5 h) [23, 24], thus favoring the degradation of valuable thermolabile compounds that can be found in mushrooms.

On the other hand, hydroalcoholic extractions have been also widely used for the recovery of high-added value compounds from mushrooms. This technique requires a moderate temperature (T = 25–60 °C). However, it needs long treatment times (t = 1–24 h) and high concentrations of solvents (from 30 to 98.6 %) [23, 24]. Moreover, hydroalcoholic extraction involves the use of high cost solvents (i.e., ethanol) and it is difficult to recycle the remaining residues.

Conventional organic solvent extraction using chloroform–methanol 2:1 (v/v), maceration (soaking), percolation, countercurrent extraction, pressurized liquid extraction, and Soxhlet

have been used to extract nutritionally valuable compounds from plant materials [25]. However, conventional extraction techniques usually imply the use of large amounts of solvents, and the risk of thermal degradation (over 100 °C) or transformation of molecules of interest remains important [25]. At this stage of development, there is an increased interest for food industry to find different technologies that can improve valuable compounds extraction from mushrooms in a sustainable way.

Novel Extraction Methods

Enzyme-Assisted Extraction

Enzyme-assisted extraction is a non-conventional methodology that offers the possibility of processing with lower temperature, rather short time, less energy consumption and high extraction yield in the food industry.

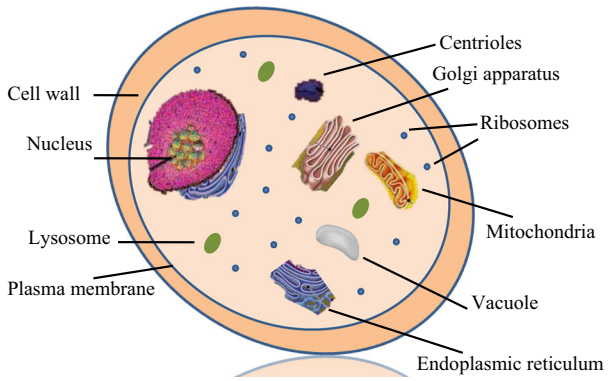

Fig. 1 Structure of a typical fungal cell and the location of some important compounds inside it

Table 3 Overall fatty acid profile (percent of total fatty acids) of some of the main mushroom species used as source of functional components

Fatty acids	*Agaricus bisporus*	*Lentinula edodes*	*Pleurotus* spp.	*Boletus edulis*	*Lactarius deliciosus*
Saturated fatty acids (SFA)					
6:0				0.07	
8:0	1.76			0.06	
10:0		2.1	18.43	0.07	
12:0		1.2		0.10	
14:0		2.0		0.18	0.48
15:0				0.23	0.53
16:0	35.0	12.2		9.84	12.08
17:0				0.31	0.18
18:0	9.0	5.1	6.50	2.72	25.33
20:0				0.34	0.44
22:0				0.54	0.38
24:0				0.24	0.60
Monounsaturated fatty acids (MUFA)					
14:1					
16:1		8.9	2.61	2.01	0.92
18:1	21.47	15.1	21.37	36.1	41.26
20:1	12.84			0.68	0.10
22:1		7.6			
Polyunsaturated fatty acids (PUFA)					
16:2				0.2	
16:3					
16:4					
18:2	13.9	13.8	49.43	42.2	17.06
18:3	0.1	13		0.17	0.26
18:4					
18:5					
20:4					
20:5					
22:5					
22:6					0.27

Adapted from [10–13]

Table 2 Macronutrients and amino acid profile of some of the main mushroom species used as source of functional components (fresh weight basis)

Mushroom class species	Proteins (g/100 g)	Essential amino acids (mg/100 g)										Carbohydrates (g/100 g)	Lipids (g/100 g)
		Leu	Val	Arg	Lys	Ile	Phe	Thr	Met	Try	His		
Agaricus bisporus/white	2.09	153	121	116	143	91	107	111	33	283	58	4.50	0.33
Agaricus bisporus/brown	2.07	142	120	108	127	85	97	102	30	292	54	4.60	0.31
Lentinula edodes	1.80	133	124	127	122	79	91	98	29	265	56	5.80	0.31
Pleurotus ostreatus	1.97	139	112	179	126	82	111	106	35	219	65	5.00	0.35
Boletus edulis	7.39	58	–	54	217	48	104	19	41	–	0.44	–	1.70
Lactarius deliciosus	2.96	–	–	–	–	–	–	–	–	–	–	6.26	0.22

Adapted from [8, 9]

Leu leucine, *Val* valine, *Arg* arginine, *Lys* lysine, *Ile* isoleucine, *Phe* phenylalanine, *Thr* threonine, *Met* methionine, *Try* tryptophane, *His* histidine

Table 4 Some of the main vitamins found in mushroom species used as source of functional components

Mushrooms species	Vitamins (mg/100 g fresh weight)									
	B_1	B_2	B_3	B_5	B_6	B_9 (μg)	B_{12} (μg)	C	D (μg)	E
Agaricus bisporus	0.03–0.19	0.04–0.62	3.607	1.497	0.04–0.10	17	0.04	2.1	0.2	
Lentinula edodes	0.05	0.07–0.22	14.1	21.879	0.965	163		3.5	3.9	
Pleurotus spp.	0.07	0.12–0.21	5.0	1.3	0.1-	27				
Boletus edulis	0.105	0.092	6.07	2.64	0.051	290		4.21	200	

Adapted from [5, 7, 14–16, 18, 19]

The cell walls of some mushrooms (shiitake mushroom) are mainly composed of the polysaccharides chitin (β-1,4-*N*-acetylglucosamine) and glucans (β-1,3 and β-1,6), which can be degraded by hydrolytic enzymes containing either chitinase or glucanase activity [26]. Hence, enzymes involved in the breaking of bonds between the polymers in fungal cell walls could be used for the intensification of the extraction. For example, a multicomponent carbohydrase preparation originating from *Trichoderma harzianum* has been used for the extraction of the bioactive compound eritadenine [27]. Eritadenine (a purine alkaloid) is a cholesterol reducing agent in shiitake mushrooms. An enzyme mixture composed of various α- and β-glucanases, but also some side activities like chitinases and proteases was used. This enzyme mixture showed a fairly high activity at pH 4.8 and 50 °C. Results showed that pre-treatment of mushrooms with hydrolytic enzymes before methanolic extraction resulted in an insignificant increase in the amount of eritadenine released. These results indicated the potential for delivery of therapeutic amounts of eritadenine from the ingestion of extracts or dried concentrates of shiitake mushroom strains.

Other enzymes (cellulase, pectinase, protease) can also hydrolyze the cellulose, pectin and crude protein, and break down the cell walls. Enzyme-assisted extraction technology of polysaccharides was performed for the extraction of polysaccharides from *Ganoderma lucidum* [28]. The optimal extraction conditions were shown as follows: complex enzyme (cellulase/pectinase/protease) amount of 3 %, extraction temperature at 45 °C, extraction time of 3 h, and extraction at pH 7. Under these conditions, the experimental amount of extract was 8.9 %, and the polysaccharides yield was 1.1 %. Another study has shown the positive effect of enzyme by comparing this technology to microwave- and hot water boiling-assisted extraction [29]. The extraction effect of a mixture of cellulase/pectinase/protease (1/1/1, w/w/w) on the polysaccharide content from *Clitocybe maxima* stipe was compared and optimized (hydrolysis and extraction conducted for 96 min at 47 °C and pH 4.64). Results showed that the extraction yield and the polysaccharide amount were significantly different: 5.86 and 40.23 % for hot water extraction, 9.4 and 52.62 % for microwave-assisted extraction, 10.26 and 53.13 % for enzyme-hydrolysis extraction, respectively. Another interesting point to note is the reduced required time (96 min) with enzyme and the highest extract purity (53.1 %) as compared to the other extraction methods.

Pulsed Electric Fields (PEF)

Over the last years, the use of pulsed electric fields (PEF) has been shown to be promising for intracellular extraction from plant food materials [30–36], by-products [37–40], and bio-suspensions [41–43] mainly due to its ability to cause lethal damage to cells or induce sub-lethal stress by transient permeabilization of cell membranes and electrophoretic movement of charged species between cellular compartments.

The cell electroporation theory is based on the concept of transmembrane potential. Numerous experimental data prove that the cytoplasm always has a negative electric potential [the entire cytoplasmic anion producing the electric potential (φ_c) unlike the electric potential of the intercellular space (φ_e)]. This physiological potential (natural) $\mu_{ph} = \varphi_c - \varphi_e \approx 0.1$ V, influences the transport of ions and small molecules. Thus, the cell has a transmembrane electric potential and a ζ-potential (zeta potential) at the electric double layer between the external liquid and the solid surface.

For a spherical cell an applied pulsed electric field E (V/cm) generates a time-dependent transmembrane potential (TMP) u_m (t), with a rise time τ [43]:

$$u_m(t) = \alpha f d_c E \cos\theta\left(1 - e^{\frac{t}{\tau}}\right) + \Delta u_p \quad (1)$$

where $\alpha = 0.75$ is a constant (in general case the value of α value depends on the shape of the cell, e.g., $\alpha = 1$ for a rectangular cell), f is a parameter that depends on geometrical and electrical properties of a cell, d_c is a cell diameter (for the plant cells $d_c \approx$ 20–100 μm [44]), θ (rad) is the angle between a point of interest on the membrane surface and the electric field direction, and Δu_m (V) is a physiological potential of a cell.

The rise time τ can be evaluated as [45]:

$$\tau = 0.5 d_c f C_m \left(\frac{1}{\sigma_c} + \frac{1}{2\sigma_e}\right) \quad (2)$$

where C_m is the specific capacity of the membrane (the different estimations give $C_m \approx 3.5$–3.9 μF/cm^2 [46], $C_m \approx 0.1$–3 μF/cm^2 [47], $C_m \approx 0.95$ μF/cm^2 [48], $C_m \approx 0.2$–0.4 μF/cm^2 [49]), σ_c is the electrical conductivity of the cell (the different estimations give $\sigma_c \approx 0.1$–1 S/m [47], $\sigma_c \approx 0.5$ S/m [48], $\sigma_c \approx 0.05$–0.5 S/m [49]).

Finally the parameter f can be evaluated as [44]:

$$f = \frac{3\sigma_e\left(3d_m d_c^2 \sigma_c + \left(3d_m^2 d_c - d_m^3\right)(\sigma_m - \sigma_c)\right)}{2d_c^3(\sigma_m + 2\sigma_e)(\sigma_m + 0.5\sigma_c) - 2(d_c - d_m)^3(\sigma_e - \sigma_m)(\sigma_c - \sigma_m)} \quad (3)$$

where σ_e is the electrical conductivity of intracellular compartments ($\approx 10^{-3}$–10^{-4} S/m [49]), σ_m is the electrical conductivity of the membrane (the different estimations give $\sigma_m \approx 10^{-4}$–10^{-6} S/m [44], $\sigma_m \approx 10^{-10}$–$10^{-6}$ S/m [49]), and d_m is the membrane thickness (≈ 5–10 nm) [44].

The cell permeabilization or disintegration index Z can be quantified by measuring the electrical conductivity of the tissue using the following equation [31]:

$$Z = \frac{\sigma - \sigma_i}{\sigma_d - \sigma_i} \quad (4)$$

where σ is the electrical conductivity at time t (S/m), σ_i is the electrical conductivity of the intact tissue (S/m), and σ_d is the electrical conductivity of the completely damaged tissue (S/m). The application of this equation gives $Z = 0$ for an intact tissue and $Z = 1$ for a completely damaged tissue.

The value of Z can be used for characterization of the recovery of intracellular compounds such as bioactive compounds, as they are located in different cell substructures, and their extraction is highly dependent of cell damage.

An example of typical pulsed electric field system is represented in Fig. 2. It is mainly composed of three parts: a pulse generator, a treatment chamber, and a pumping system to handle the product. The system is generally controlled and monitored by an oscilloscope and a computer. The pulse generator is running basically on DC high voltage associated with a pulse forming unit and, occasionally, a pulse transformer to increase the voltage. The treatment chamber contains basically two electrodes (high voltage and ground) separated by insulating material. Direct current electric pulses of high voltages (up to 40 kV) for a very short time (<10 ms) allow the extraction of selectively high-added value compounds from complex matrices without degrading the material [50]. Two configurations are usually used: a batch system or continuous flow mode. The gap fixed between the electrodes reflects the intensity of the electric fields (most often below 10 kV/cm) applied to the material being processed. When performing PEF-assisted extraction experiments, not only the electric field strength, the pulse width and the repetition rate are being controlled, but also the number of pulses, the treatment time; consisting of multiplying the number of pulses by the pulse width, expressed in μs or ms, and finally the total specific energy (kJ/kg), which is generally below 20 kJ/kg [51]. The total specific energy depends mainly on the applied voltage, the treatment time, and the resistance of the treatment chamber. Several other parameters influence the PEF-assisted extraction efficiency. In fact, besides the PEF processing parameters, the extraction medium (temperature, pH, solvent type and concentration) and the physicochemical properties of the treated matrix (product size, electric conductivity, cell structure and membrane characteristics) being the most influencing [31, 51]. Moreover, the cell location (cytoplasm or vacuoles) of the targeted molecules being extracted influences the electropermeabilization procedure [50].

The impact of PEF alone and/or combined with other methodologies on the recovery of valuable compounds from mushrooms has been evaluated by different authors. For instance, the effects of PEF-assisted extraction to recover exopolysaccharides (EPS) from Tibetan spiritual mushrooms were evaluated [52]. The authors found that PEF treatment significantly enhanced EPS recovery. Moreover, it was found that under the optimal conditions (electric field intensity $E = 40$ kV/cm, number of pulses $n = 8$ and pH 7), the EPS extraction yield was increased by 84.3 %.

The efficiency of PEF-, microwave- and ultrasonic-assisted methods was compared for extraction of active components from Chinese mushroom Jew's ear [53]. These extracts have anti-coagulant effects and are applied in a Chinese herbal medicine. Highest yield of fungal polysaccharide with anti-coagulant activity was observed for PEF-assisted technique at field strength of 24 kV/cm.

In a different study, the effects of PEF (100–1000 V/cm) alone and/or combination with pressure for proteins, polyphenols and polysaccharide's recovery from mushrooms (*Agaricus bisporus*) were recently investigated [54]. Pressure extraction (PE) was done using the laboratory-

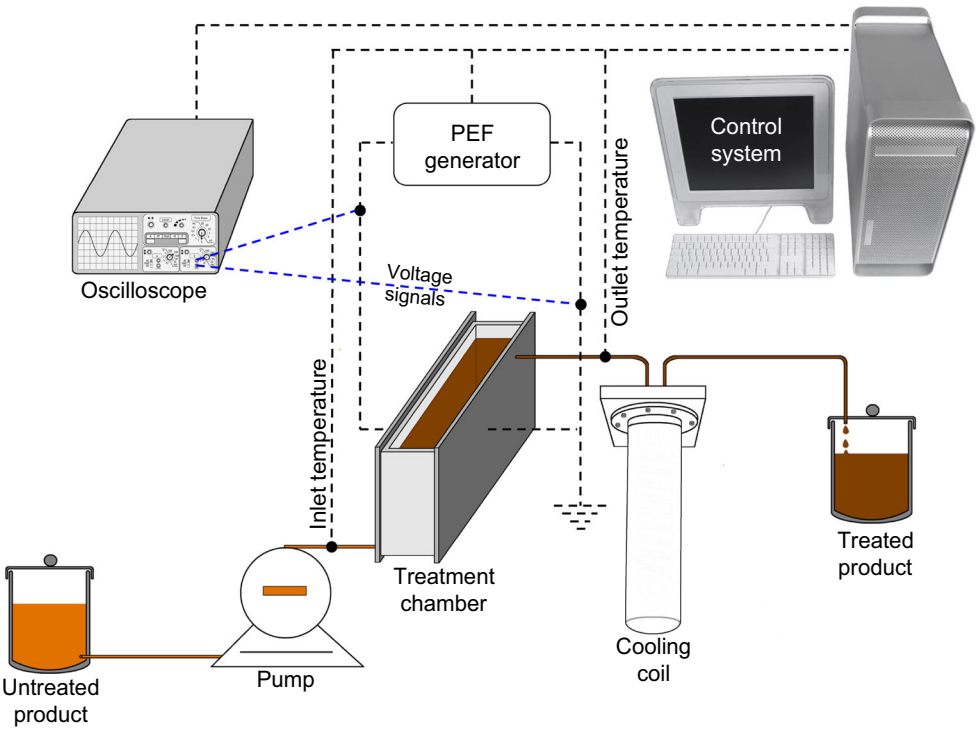

Fig. 2 Schematic representation of a pulsed electric field (PEF) system

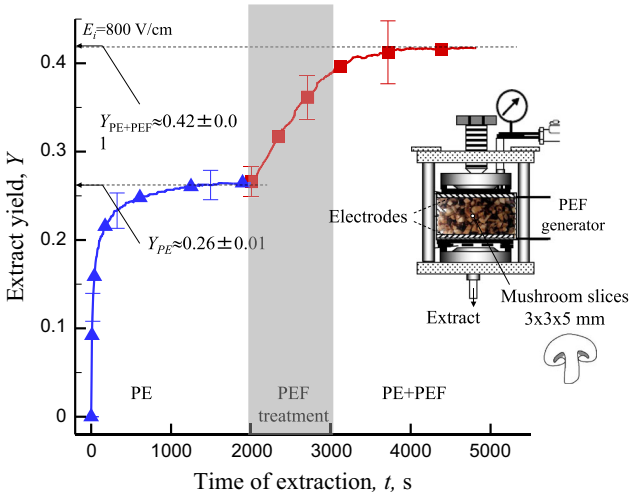

Fig. 3 Extract yield, Y (=mass of extract/initial mass of the sample), versus time of extraction, t. The applied pressure was $p = 5$ bar. The bipolar *near-rectangular pulses* with pulse duration of 1000 μs were used. The initial electric field strength was $E_i = 800$ V/cm and the total time of PEF treatment was $t_{PEF} = 0.4$ s. The PEF treatment was started after 2000 s of pressing and was applied during the 1000 s of pressing (*dashed area*) (compiled from [54, 55] with permission)

pressing cell, equipped with a PEF treatment system. Figure 3 shows the example of the pressing curve for electric field strength of 800 V/cm. For conventional pressure extraction without application of PEF, the maximum yield of extract was $Y_{PE} \approx 0.26$. The PEF-assisted extraction gave the highest yield of extract, $Y_{PE+PEF} \approx 0.42 \pm 0.01$ [54, 55].

Moreover, the results were compared with hot water extraction (WE, 70 °C, 2 h) and ethanol extraction (EE, 25 °C, 24 h). The method of WE gave relatively high contents of proteins, total polyphenols and polysaccharides. However, the extracts were cloudy and their colloid stability was low. This method did not allow preservation of the fresh protein quality, and the proteins were presumably in the coagulated state. The extracts produced using EE method were also cloudy and unstable.

These authors concluded that at temperature $T = 343$ K the relative extraction, A/A_m, of valuable compounds from mushrooms after applying PEF can be explained by the first-order kinetic law [54]:

$$\frac{A}{A_m} = 1 - e^{\left(\frac{\tau_e}{t}\right)} \quad (5)$$

Here, A represents the absorbance of the extract (1/10 dilution, $\lambda = 260$ nm) at time t, A_m corresponds to the maximum absorbance of extract, obtained at long time of extraction ($t \approx 2$ h) and τ_e is the characteristic time of extraction.

PEF-assisted pressure extraction gave clear extracts with high colloid stability. It was concluded that PEF was a suitable technology for the recovery of valuable compounds in the used conditions, because PEF increased the selective extraction of nutritionally valuable compounds mainly due to cell permeabilization obtaining clear extracts with high colloidal stability, thus facilitating the separation and the purification processes after extraction in

comparison with conventional hot water and ethanol extraction. Moreover, it was found that the combination of PEF with pressure extraction gave higher nucleic acid/proteins ratio as compared with that of pressure extraction alone. In addition, PE + PEF allowed production of mushroom extracts with high contents of fresh-like proteins and polysaccharides.

Ultrasound-Assisted Extraction (UAE)

Ultrasound-assisted extraction (UAE) has attracted much interest in recent years due to their many advantages in the recovery of valuable compounds from different matrices compared to conventional extraction methods [56–58]. In the ultrasonic process, mushroom cells are disrupted by shock waves from cavitation bubbles, thus facilitating mass transfer hence an absolute increase in the extraction yield and kinetics. In addition, the recovery of valuable compounds from plant food materials assisted by ultrasounds is an inexpensive and simple method [59]. This technique can be combined with solvents and allows to decrease the extraction time and the temperature of the extraction, which can be a potential tool for the preservation of thermolabile compounds [59].

UAE has been widely used by several authors to extract nutritionally valuable compounds from mushrooms [60–63]. Table 5 summarizes some studies applying UAE to extract high-added value components from mushrooms.

In this line, it was revealed that pulsed countercurrent ultrasound-assisted extraction demonstrated the best extraction yield with significant short time (40 min less), higher yield of polysaccharides (1.5 % more) at 16:1 liquid–solid ratio at lower temperature (30 °C lower) than hot water extraction [61]. In addition, introduction of ultrasonic probe and concurrency increased the mass transfer and effective contact surface between solid and liquid therefore a better yield than those by normal ultrasonic extraction was observed [61]. In another study, it was indicated that UAE promoted the extraction of bigger molecules like polysaccharides from mushroom compared with those from hot water extraction (52–129 % increase) [62]. Response surface methodology was used to optimize the UAE of polysaccharides from *Trametes orientalis* [60]. Even though positive indication was shown by using UAE, most of these studies generalized the application power of ultrasound without discussing about the power density and adsorbed power during the extraction which are essential parameters to monitor UAE process [58, 64].

In another study, the optimal UAE conditions to recover polysaccharides from black fungus were studied. It was concluded that ultrasounds treatment at 350 W, solid–liquid ratio 1/5, and 35 min of extraction time at 90 °C

Table 5 Ultrasound-assisted extraction (UAE) of nutritionally valuable compounds from some mushroom species

Mushroom	Treatment conditions	Major findings	References
Ultrasound-assisted extraction (UAE)			
Trametes orientalis	Ultrasonic treatment was conducted in an ultrasonic cell disintegrator. Conditions were: (1) water (liquid–solid ratios 25–35 ml/g); (2) ultrasonic power (80–120 W); (3) temperatures (30–50 °C); (4) times (30–50 min)	The optimal extraction conditions were: water (liquid–solid ratio 30.6 ml/g, ultrasonic power 109.8 W, temperature 40.2 °C, and time 42.2 min. Polysaccharide content was 7.47 % at optimal extraction condition	[60]
Boletus edulis	Ultrasonic clearer extraction (UCE): 20–90 °C, 20 kHz power. Static probe ultrasonic extraction (SPUE): 20–90 °C, 20 kHz ultrasonic probe Pulsed countercurrent probe ultrasonic extraction (CCPUE): countercurrent (pulse duration 4 s) provided by two peristaltic pumps, 20–90 °C, 20 kHz ultrasonic probe Hot water extraction (HWE): 20–90 °C with constantly stirring at 500 rpm	Liquid to solid ratio was optimized at 16:1 in every condition. The optimal condition for extraction was CCPUE at 60 °C for 40 min and liquid–solid ratio 16:1, which yielded 8.21 % polysaccharides	[61]
Grifola frondosa and *Lentinus edodes*	Mushroom sample was dried, grinded and screened (<250 μm). Ultrasonic probe (20 kHz, 130 W, 12 mm diameter) with power density 0.33 W/ml liquid was used. 3 g of powder were extracted in 90 ml water at 45–50 °C. Extraction time varied from 1 to 60 min. 45 °C water extraction was used as a comparison	Relationship of total extract yields from mushroom and extraction time which was fitted into three models: power law, Weibull's exponential and Elovich's logarithmic model. Relationship of polysaccharides yield and extraction time did not fit any model. Total extract yields were around 55 % (w/w) after 60 min extraction and polysaccharides yield from *G. frondosa* was 0.05 %, and yield from *L. edodes* was 0.13 %. After UAE, the particle structure was more porous	[62]

allowed to obtain the maximum polysaccharide yield [65]. Moreover, the recovery of polysaccharides from *A. bisporus* mushrooms was also studied. The optimal conditions to extract the maximum polysaccharide content from this type of mushroom using UAE were ultrasonic power 230 W, at $T = 70$ °C for $t = 62$ min [66]. At these conditions, a highest *A. bisporus* polysaccharides yield of 6.02 % was achieved. It was also indicated that extracted polysaccharides have good antioxidant activity, e.g., at 250 μg/ml concentration, mushroom polysaccharides were observed to possess significantly higher (86.1 %) free radical-scavenging activity when compared to reference. The effect of ultrasound-assisted extraction on melanin recovery from dried fruit bodies of *Auricularia auricula* (*A. auricula*) was evaluated [67]. The optimal conditions were obtained following ultrasound power 250 W, $T = 63$ °C, a liquid–solid ratio of 43 ml/g and a duration of 36 min. Under these conditions, two extractions sufficiently reached the maximal melanin yield (120.05 mg/100 g). Moreover, in another study, it was also determined the proximate composition, total phenolic compounds, antioxidant capacity and antimicrobial activities of different extracts of *Laetiporus sulphureus* [68]. Optimum extraction methodologies (classical and ultrasound-assisted) provided one fraction containing neutral and polar lipids and the other fraction containing fungal carotenoids and pigments. Fatty acid analysis indicated a predominant level of polyunsaturated fatty acids followed by saturated and mono-unsaturated fatty acids. Both the aqueous methanolic and water extracts contained higher TPC and showed better antioxidant capacity than the ethanolic extract. Irrespective of the type of extraction applied, *L. sulphureus* showed good antimicrobial activity against all the tested bacteria and fungi, being in some cases stronger than the used antibiotics and mycotics.

Microwave-Assisted Extraction (MAE)

Microwave-assisted extraction (MAE) is a process that includes heating the material causing moisture to evaporate, which generates tremendous pressure and the rupture of cells facilitating the release of the desired intracellular contents [58]. The electromagnetic spectrum of microwave ranges between far infrared light and radio frequencies. The frequency range is situated from 300 MHz to 300 GHz, corresponding to 1 m–1 cm wavelength range. For industrial and scientific microwave heating, 915 ± 25, 2450 ± 13, 5800 ± 75 and 22,125 ± 125 MHz, are the most applied frequencies [69]. The heating effect of microwaves is mainly associated with the dielectric properties of materials. Two parameters: the dielectric constant and the dielectric loss defined these properties. The ability of a molecule to be polarized by the electric field is symbolized by ε, namely the former. When processing at low frequencies, the maximum amount of energy is stored by the material and given by ε. The efficiency of converting the electromagnetic radiation energy into heat is measured by the dielectric loss ε'. When the dielectric constant decreases, the dielectric loss increases [70]. The ratio between the dielectric loss and dielectric constant represents the dissipation factor symbolized by tan δ.

Materials that are transparent to microwave energy have an infinite penetration, whereas reflective ones (e.g., metals) have a zero penetration. The half-power depth is considered as one of the efficient ways to characterize penetration. This parameter characterizes the distance at which the power density is reduced to the half from the sample surface and varies not only with the sample's dielectric properties but also slightly with the inverse of the square root of the frequency. The power absorption is then given by the Lambert's expression described in Eq. (6).

$$P = P_0 e^{-2\alpha' d} \tag{6}$$

In this equation, P_0 and P represent the incident power and the power at the penetration depth, respectively. α' and d represent the attenuation factor and the penetration depth, respectively [69].

Depending on the electric field strength's local time-average and the dielectric properties, the dissipated power in a medium is given by Eq. (7) [71].

$$\frac{P}{V} = 2\pi f \varepsilon_0 \varepsilon'' |E|^2_{\text{rms}} \tag{7}$$

where ε_0 represents the permittivity of the free space (8.85×10^{-12} F/m), and ε'' represents the imaginary part of the relative permittivity or 'loss factor'. P, f, $|E|_{\text{rms}}$, and V represent the power (W), the frequency (Hz), the root-mean-square electric field (V/m), and the volume (m^3), respectively.

Fundamental difference hence exists between conventional heating and microwave. In fact, the heat transfer is occurring differently; from the heating device to the medium in conventional heating, and by dissipation inside the irradiated medium in microwave heating. The Fourier heat equation contains thus an extra term, reflecting this difference, given by Eq. (8) [71].

$$\rho C_P \frac{\partial T}{\partial t} + \kappa \nabla^2 T + \frac{P}{V} = 0 \tag{8}$$

where ρ, C_P, κ, T and t represent the specific density (kg/m), specific heat capacity (J/kg/K), thermal conductivity (W/m/K), temperature (K), and time (s), respectively.

Microwaves heat up the molecules by ionic conduction and dipole rotation. If the extraction medium offers a resistance to the ion migration, a friction is generated and the minute microscopic traces of moisture occurring in the

sample are heated. This process generates tremendous pressure on the cell wall until rupture and release of active compounds from the sample. In this case heating occurs only in a selective and targeted material; consequently, there is no heat release into the environment [72–74]. This technique, widely used in the extraction of bioactive compounds, provides a rapid sample preparation with reduced amounts of solvent.

There are several studies which have shown the higher efficiency of MAE to recover nutritionally valuable compounds from mushrooms in comparison with other conventional technologies [75]. Table 6 summarizes most of the performed studies [29, 75–83].

MAE showed obvious advantages of high extraction efficiency from *Terfezia boudieri Chatin*, *Boletus edulis*, and *Lactarius volemus* with lower solvent consumption in terms of high antioxidant capacity/activity of extracts achieved within the shortest time [75]. Authors found that methanol concentration ≈80 %, extraction temperature 80 °C, and extraction time ≈5 min were the optimal extraction conditions. They found that high contents of phenolic and flavonoid compounds were the major contributors to the observed high antioxidant activities of these extracts.

In another study, it was shown that microwave-based DNA extraction method for subsequent DNA amplifications by PCR on mushrooms of different *Agaricomycetes* requires tiny amounts of fungal material, is rapid and achieved within minutes [84], that is why MAE is superior to classical extraction methods which are work intensive and require larger amounts of starting material and hours of time for performance [84]. In addition, specific expensive and hazardous chemicals for cell lysis and DNA purification were utilized for conventional extraction. The authors showed that microwave method with highest reliability (≈90 %) was suitable for vegetative mycelium harvested from fresh and also from aged fungal cultures. Another author utilized MAE technique for isolating the fungal metabolite ergosterol from mushrooms (*A. bisporus*) [76]. It was found that MAE-derived ergosterol values were comparable to those obtained by classical solvent extraction and significantly exceeded those obtained by supercritical fluid extraction (SFE). However, MAE procedure is simple, rapid, reliable, and economical with respect to amounts of reagents required, especially when compared with classical solvent and SFE.

On the other hand, nine kinds of mushrooms including *Hazel*, *Slippery*, *Shiitake*, *Hericium erinaceu*, *Citrinopileatus*, *Flammulina,* *Comatus*, *Tricholoma giganteum*, and *Xian* mushrooms were used for MAE nicotine extraction [83]. They found that the optimal high-throughput dynamic microwave-assisted extraction (HTDMAE) conditions were as follows: the extraction solvent was water, the microwave power was 1000 W, the extraction solvent volume was 18 ml, and the extraction solvent flow rate was 2 ml/min. It was found that under optimal conditions of HTDMAE, nicotine yield was 34.9 μg/kg; which was 1.29 times higher than that obtained for solvent extraction and even 1.14 times higher than for pressurized microwave-assisted extraction. The extraction effect on the polysaccharide of *C. maxima* stipe was compared, and the extraction conditions were optimized [30]. With three of the above mentioned mushrooms, the extraction yield and the polysaccharide amount were greatly different, which were 5.86 and 40.23 % for hot water extraction, 9.4 and 52.62 % for microware-assisted extraction, 10.26 and 53.13 % for complex–enzyme–hydrolysis extraction, respectively.

Microwave-assisted extraction technique has been employed for the extraction of polysaccharides from *Agaricus blazei* Murrill [77]. The optimum conditions for a 12.35 % recovery were: 29.37 min extraction time, 400 W microwave power, 74.64 °C extraction temperature and 32.7:1 ratio of water to material. In the case of *Cordyceps militaris*, the optimal conditions to obtain the highest polysaccharide yield were a microwave power of 744.8 W for 4.2 min and a ratio of solution to solid of 31.1 ml/g [78]. Similarly, three polysaccharide fractions were separated from *Lycoris aurea* [79]. The microwaves technique can be hyphenated with ultrasound-assisted extraction in order to reduce the extraction time, increase the efficiency and save the energy. The experimental results confirmed that ultrasonic/microwave-assisted extraction (UMAE) of polysaccharides had great potential and efficiency compared with traditional hot water extraction. This coupled method was employed for the separation of polysaccharides from *Lycium barbarum* at the following optimized operating conditions: microwave power of 500 W for 10 min and ultrasonication for 30 min at 50 °C and pH 9 [80].

In the case of polysaccharides from *G. lucidum*, the optimal extraction conditions were 50 W ultrasonic power, 284 W microwave power, 701 s extraction time and 11.6:1 water/solid ratio [81]. Using this coupled method, the yield of polysaccharides could be significantly improved compared with that of classical hot water extraction, reaching nearly 100 % yield, and increased by 27.7 % compared to ultrasound-assisted extraction. Polysaccharides were also separated from *Inonotus obliquus* by microwave and ultrasound-assisted extraction at 90 W microwave power with 40 kHz ultrasonic frequency, and 1:20 (w/v) solid–water ratio for 19 min [82]. Under these conditions, the recovery and purity of polysaccharides were 3.25 and 73.16 %, respectively, which are above those of traditional hot water extraction.

Besides the degradation risks caused by traditional water extraction, this method requires high-energy demands compared to heating by microwaves [85]. In fact, it has been

Table 6 Microwave-assisted extraction (MAE) of nutritionally valuable compounds from some mushroom species

Mushroom	Treatment conditions	Major findings	References
Microwave-assisted extraction (MAE)			
Clitocybe maxima	The fresh stipe was washed, oven dried and grinded through 20 mesh. 5 g of powder were extracted in 200 ml of distilled water at 600 rpm, 90 °C for 4 h. 5 g of powder were extracted in 125 ml of distilled water at 600 r/min, 90 °C for 2 h. Microwave power was 540 W for 8 min. 5 g of powder were mixed with 1 % complex enzyme (cellulose/pectinase/protease = 1:1:1), distilled water was added at the solid–liquid ratio of 1:25, hydrolysis and extraction was conducted for 96 min at 47 °C and pH 4.64	For microwave-assisted extraction (MAE), total yield of polysaccharide was 9.24 %, which is 57.8 % higher than using water extraction. Polysaccharides generated by MAE were more pure than using HWE	[30]
Terfezia boudieri Chatin, *Boletus edulis*, and *Lactarius volemus*	Dried sample (0.2 g) was extracted with 20 ml methanol/water (80:20, v/v) at 80 °C for 5 min after 3 min temperature balancing time, and a microwave power of 0–1500 W. Extracts were filtered through a filter paper, then through 0.45 μm syringe filters	The optimal extraction conditions were: methanol concentration of 80 %, extraction temperature of 80 °C, and extraction time of 5 min. The methanolic extracts of wild edible mushrooms obtained after using microwave-assisted extraction (MAE) were highly effective and advantageous among the extraction techniques	[75]
Agaricus bisporus	Samples were frozen in liquid nitrogen, grinded and freeze dried. Irradiation of milligram-sized samples in a conventional microwave oven for 35 s in the presence of methanol and aqueous sodium hydroxide and results in simultaneous extraction and saponification	MAE-derived ergosterol values to be comparable with those obtained by classical solvent extraction and to significantly exceed those obtained by supercritical fluid extraction	[76]
Agaricus blazei Murrill	Samples were air-dried in an oven at 40 °C and grinded into a fine powder. MAE parameters were the following: power 200–400, t = 20–40 min, T = 60–70 °C, solid to liquid ratios 1/20–1/40. Maceration extraction: 5.0 g of powder was mixed with 100 ml water and macerated at 25 °C for three 12 h. UAE 5.0 g was extracted in 100 ml water with ultrasonic power of 100 W at 25 °C for three 40 min	The MAE optimum conditions were t = 29.37 min, microwave power 400 W, T = 74.64 °C and solid–liquid ratio 1/32.7 with an enhanced yield of 12.35 %. The scavenging effect was 16.5–82.7 % for PMAE At the concentration of 0.2–8.0	[77]
Cordyceps militaris	*Cordyceps militaris* dried powder was grinded. 1 g of the dried powder was extracted twice with hot water, the extract was concentrated under reduced pressure to constant volume. 1 g of *C. militaris* sample was immersed in distilled water and then, the suspensions were irradiated with microwaves. MAE power was varied from 450 to 750 W, extraction time 3–5 min, solid to liquid ratios of 1/25–1/35	The optimal conditions to obtain highest yield were microwave power of 744.8 W, an extraction time of 4.2 min and solid–liquid ratio of 1/31.1	[78]
Lycoris aurea	MAE parameters were: T = 80–100 °C, treatment time 10–20 min and solid to liquid ratios of 1/60–1/100	The extract obtained after 20 min at 100 °C of MAE had higher purity 70.82 % than that obtained after traditional extraction 63.54 %. The polysaccharide extraction yield was increased by 1.25 times after MAE	[79]

Table 6 continued

Mushroom	Treatment conditions	Major findings	References
Lycium barbarum	Sample was dried and grinded. Soxhlet extraction was performed by mixing powder with 200 ml water for 40–300 min	The parameters of MUAE were optimized: microwave power of 500 W, microwave time of 10 min, ultrasonication time of 30 min, ultrasonication temperature of 50 °C and pH 9.0	[80]
Ganoderma lucidum	Ultrasonic/microwave extraction procedure were carried out at a microwave power of 116–284 W, ultrasonic power of 50 W and ultrasonic frequency of 40 kHz. The pellet of *G. lucidum* powders was dispersed in 100 ml flask in water to solid ratios (ml/g) of 11.6:1, 15:1, 20:1, 25:1 and 28.4:1	The optimal extraction conditions were ultrasonic power of 50 W, microwave power of 284 W, extraction time of 701 s and water/solid ratio of 11.6:1. Polysaccharidés yield was 115.56 % after UMAE above that of HWE and 27.7 % higher compared to ultrasound-assisted extraction	[81]
Inonotus obliquus	Grinded *I. obliquus* samples were refluxed twice with ethanol at 70 °C and then vacuum-dried at 60 °C for 12 h. 5 g of powder were mixed with water and UMAE procedure was done at microwave power 55–115 W, extraction time of 15–25 min and solid–liquid ratios 1/15–1/25. HWE was held out at $T = 100$ °C, extraction time of 240 min, and solid–liquid ratio of 1/20	UMAE optimal conditions were 90 W microwave power, 50 W ultrasonic power together with 40 kHz ultrasonic frequency, solid–liquid ratio was 1/20 (w/v) and the extracting time was 19 min. Polysaccharidés yield and purity were 3.25 % and 73.16 %, respectively, which are above that of traditional hot water extraction	[82]
Hazel mushroom, *Slippery* mushroom, *Shiitake* mushroom, *Hericium erinaceu, citrinopileatus, Flammulina, Comatus, Tricholoma giganteum*, and *Xian* mushroom	Samples were dried at 60 °C, powdered and sieved through a 40 mesh sieve, then stored in a sealed brown bottle at room temperature. High-throughput dynamic microwave-assisted extraction (HTDMAE) was held out at 200–1000 W microwave power, extraction solvent volume 10–30 ml and extraction solvent flow rate 1–3 ml/min	The optimal HTDMAE conditions were as follows: the extraction solvent was water, the microwave power was 1000 W, the extraction solvent volume was 18 ml, and the extraction solvent flow rate was 2 ml/min	[83]

MUAE microwaves-ultrasound-assisted extraction

reported that coupling conventional method such as hydrodistillation with microwaves, leads to the reduction in the energy cost by almost twofold compared to hydrodistillation alone; decreasing thus from 0.12 kWh/kg (430 kJ/kg, $6/t) to 0.07 kWh/kg (270 kJ/kg, $3.5/t) [86].

Moreover, microwave heat transfer is much faster than conventional one, as it is not limited to thermal conduction or convection currents, and the maximum temperature is only dependent on the rate of heat loss and power applied [71].

Subcritical and Supercritical fluid Extraction

In recent decades, both subcritical and supercritical fluid extraction techniques have emerged as useful tools to replace conventional extraction methods. These techniques are considered environmentally friendly and have the potential to provide higher extraction yields of nutritionally valuable compounds from different sources, including mushrooms compared to classic extractions [87].

Subcritical Water Extraction (SWE)

SWE, also referred as hot pressurized water extraction, is a technique that consists in using hot water (from 100 to 374 °C, the latter being the water critical temperature) under high pressure to maintain water in the liquid state. The most important factor to consider in this type of extraction procedure is the variability of the dielectric constant with temperature [55]. At low temperature, compounds with high polarity easily solute in water while super-heated water (above 100 °C) can act as organic solvent and solute lower polar compounds [88].

Figure 4 illustrates the semi-continuous prototype SWE apparatus to extract hydrophilic compounds from *G. lucidum*, adapted from Askin et al. [89]. Table 7 summarizes the results of application of SWE technique for the extraction of nutritionally valuable compounds from mushrooms [89–93].

The impact of temperatures (100–300 °C), and extraction apparatuses (batch and semi-continuous) on extracting

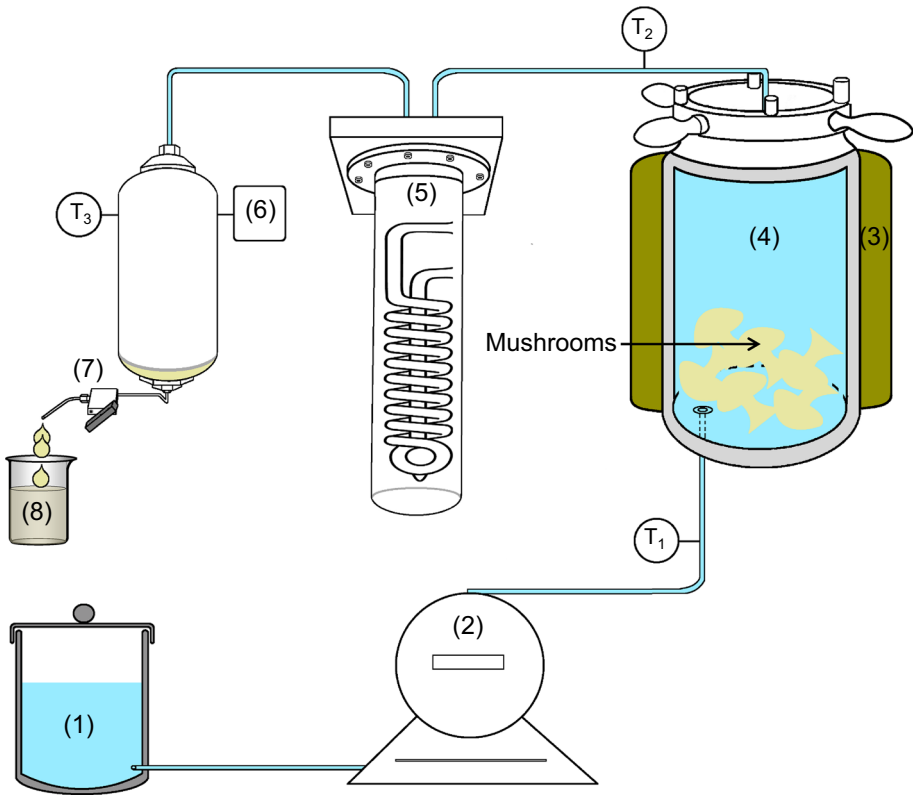

Fig. 4 Schematic representation of SWE semi-continuous apparatus. *1* water reservoir, *2* water pump, *3* heater, *4* extractor, *5* heat exchanger, *6* temperature controller, *7* backpressure regulator, *8* collecting beaker. Adapted from [89]

polysaccharides from *G. lucidum* was investigated [89]. The authors suggested that the optimal temperature for extracting water-soluble polysaccharides was 200 °C at which up to three times more of soluble content was extracted in batch system and up to nine times more in the semi-continuous system [89]. In another work, subcritical water extraction was used to recover bioactive compounds from golden oyster mushroom with high temperatures (50–300 °C) and different pressures (0.002–5 MPa) and it was revealed that extracts possessed higher antioxidant activities when higher temperatures (250–300 °C) and longer times were used. Moreover, the effects of subcritical water to recover antioxidant compounds from medicinal mushroom Chaga mushroom (*I. obliquus*) under similar conditions to the above mentioned were also studied [91]. The authors obtained the highest antioxidant activities when SWE was applied under 250 °C.

SWE application on mushroom remains untapped. Studies so far mostly focused on extracting phenolic and polysaccharides from mushroom by SWE. However, the success of extracting essential oils from herbs by subcritical water [94] might also indicate that compounds with low polarity (i.e., fatty acids) from mushroom by subcritical water is worthy of investigating. In addition, the modeling kinetics between pressure/temperature of SWE and bioactive compounds are also interesting to study because manipulation of pressure and temperature indicates the change of water polarity, which might to different extraction outcomes.

The suitability of pressurized water extraction (PWE) of crude polysaccharides as secondary metabolites from *Lentinula edodes* was investigated [95]. A series of experiments were carried out to examine the effects of extraction times and pressures. The results indicated that the maximum recovery of polysaccharides was about 90 % of the crude polysaccharides from mycelia pellets when the pressure was at 10.1 MPa for 70 min (28 °C). This was a drastic improvement over that of boiling water extraction (BWE) at 0.1 MPa for 40 min, which gave only 27.9 % recovery. A nitroblue tetrazolium (NBT) reduction assay was used to examine the macrophage stimulating activities (MSA), and it was found that the PWE polysaccharides retained the MSA. The morphology of the macrophage cells treated by PWE polysaccharides was also examined and found to be similar to that of the positive control lipopolysaccharides treated. Finally, gel chromatographic and NMR experiments revealed that both PWE and BWE polysaccharides showed the presence of four similar molecular mass components and the α-(1 → 4)-D-Glcp and β-(1 → 6)-D-Glcp linkage residues. The improved PWE efficiency is probably due to the possibility that under high pressure, the solid polysaccharide's hydrogen binding is partially destroyed to increase structure elasticity and water solubility [95].

Table 7 Subcritical and supercritical fluid extraction of nutritionally valuable compounds from mushrooms

Mushroom	Conditions	Results	References
Subcritical water extraction (SWE)			
Ganoderma lucidum	Dried *G. lucidum* (<3 mm particle size); batch system (0.5 g sample/5 ml water, 100–300 °C for 60 min); semi-continuous system (4.46 g sample, 100–200 °C, 10 MPa, 1 ml/min flow rate for 130 min)	Highest yield by batch system: 328 mg WSOC/g dried sample at 200 °C/60 min. Highest yield by semi-continuous system: 0.44 mg β-glucan/100 dried sample and 241 mg WSOC/g dried sample at 200 °C, 1 ml/min for 130 min. Molecular weight distribution ranged from 500 to 1400 g/g mol in all the SWE powder. Polysaccharides with $n \leq 21$ were considered to be extractable at the optimum conditions	[89]
Golden Oyster mushroom	20 mg powdered mushroom (<500 μm) was placed in the reaction vessel equipped with 10 ml subcritical water (50, 100, 150, 200, 250, and 300 °C and 0.002–5 MPa pressure) and extracted in various time lengths (10, 30, and 60 min)	Highest total phenolic content: 98.39 μg GAE/ml at 250 °C/60 min and 98.58 μg GAE/ml at 300 °C/30 min. Highest β-glucan content: 12.84 % at 200 °C/60 min. Highest DPPH RSA: 88.49 % at 250 °C/60 min and 86.47 % at 300 °C/30 min. Highest ABTS RSA: 67.59 % at 300 °C/60 min. Highest reducing power: 1.083 at 250 °C/60 min and 1.077 at 300 °C/30 min	[90]
Chaga mushroom	20 mg powdered mushroom (<710 μm) was placed in the reaction vessel equipped with 10 ml subcritical water (50, 100, 150, 200, 250, and 300 °C and 0.002–5 MPa pressure) and extracted in various time lengths (10, 30, and 60 min)	Highest total phenolic content: 10.72 μg GAE/g sample at 250 °C/30 min. Highest SOD activity: 92.3 % at 250 °C/60 min. Highest DPPH RSA: 72.5 % at 250 °C/60 min. Highest ABTS RSA: 97.8 % at 250 °C/60 min. Highest reducing power: 1.048 at 250 °C/30 min	[91]
Grifola frondosa	Temperature ranged from 130 to 240 °C, reaction time ranged from 5 to 55 min, liquid–solid ratio (ml/g) ranged from 16:6:1 to 33.4:1, and pressure was fixed at 5 MPa	Optimized conditions were 210 °C/43.65 min, and liquid to solid ratio of 26.15:1. 25.1 % polysaccharides were obtained under the optimum conditions. The extracts obtained after SWE yielded two times more polysaccharides than traditional hot water extraction	[92]
Ganoderma lucidum	Dried *G. lucidum* (<2 mm particles). Semi-continuous system: temperature ranging from 100 to 190 °C, 1 ml/min flow rate for 30 min	The mass of extracted polysaccharides distributed between 688 and 2638 *m/z*. The water-soluble compounds were consisted of polysaccharides with β-glucan as backbone. SWE promoted the release of more extractable polysaccharides	[93]
Supercritical fluid extraction (SFE)			
Lentinula edodes	Dry shiitake (0.214 mm); 100 % CO_2—SFE, SFE and organic solvent mixtures versus classic solvent extraction	Highest yield with 3.81 % lipid compounds w/w: SFE (40 °C/20 MPa) + 15 % ethanol. Highest DPPH RSA: ethyl acetate extraction and SFE (40 °C/20 MPa) + 15 % ethanol. Highest total phenolic content: ethyl acetate extraction. Antimicrobial activity: extract from SFE is more effective especially on gram positive microorganism, compared with the extract obtained from classic solvent extractions	[100]
Agaricus brasiliensis	Dried *A. brasiliensis* (6.6 % MC); pure CO_2 SFE (40–60 °C, 10–30 MPa, 3.5 h, 12 ± 2 g CO_2/min flow rate); co-solvent SFE (2.5–10.0 % EtOH); Soxhlet extraction 5 g sample/150 ml of DCM, Hx, DCM, water, EtAc); cold maceration (7 days, 50 g sample/200 ml EtOH); hydrodistillation (50 g sample/700 ml water, 6 h)	Highest total yield: 57 % at Soxhlet (water) method. Highest pure CO_2 SFE yield: 1.19 % at 50 °C/30 MPa). Highest co-solvent CO_2 SFE yield: 4.2 % at 10 % EtOH. Highest TPC (74 mg CAE/g) and DPPH RSA were attained at cold maceration with EtOH. Pure CO_2 SFE extract TPC values: 14–32 mg CAE/g. Co-solvent CO_2 SFE extract TPC values: 18–no need 42 mg CAE/g. Antimicrobial activity: extracts by co-solvent CO_2 SFE was less effective on both *S. aureus* and *B. cereus* than those by pure CO_2 SFE	[101]

MC moisture content, *DCM* dichloromethane, *EtAc* ethyl acetate, *Hx* hexane, *EtOH* ethanol, *CAE* chlorogenic acid equivalent, *WSOC* water-soluble organic compounds, *TPC* total phenolic content, *GAE* gallic acid equivalent

On the other hand, the impact of subcritical carbon dioxide extraction on the extraction of fatty acids from *B. edulis* mushroom was investigated [96]. It was found that this method could improve the extraction yields of fatty acids as compared to conventional extraction methods.

Supercritical Fluid Extraction (SFE)

A supercritical fluid is any substance that is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. At these conditions, some fluid properties are placed between those of a gas and those of a liquid. Although the density of a supercritical fluid is similar to a liquid and its viscosity is similar to a gas, its diffusivity is intermediate between the two states, thus favoring the extraction of intracellular compounds. The diffusivity D could be calculated using the mathematical model developed by Goto et al. [97], and adapted by Mhemdi et al. [98]. The proposed model allows the estimation of the effective diffusivity D_e from the experimental data on the time dependence of extraction ratio $Y(t)$, using the simplified exponential model given by Eq. (9) [98].

$$Y(t) = 1 - e^{-\frac{15D_e t}{r^2}} \quad (9)$$

where r is a radius of solid particles, the effective diffusivity D_e can be easily obtained from fitting the plot of $\ln(1 - Y(t))$ versus 15 t/r.

SFE has been used for several applications during the last decades, especially important has been its use in food and agricultural as well as fuel industries, followed by analysis/chromatography, pharmaceuticals, environmental contaminants, metal-ion extractions and pesticides. And, the last two decades have acquired a special relevancy for the extraction of nutritionally valuable compounds such as from different sources, including mushrooms. Figure 5 was adapted from [55] who briefly illustrated the set-up of a pilot plant scale SFE using CO_2 and co-solvents in the extraction. Since under critical condition, CO_2 supercritical fluid has low solubility that indicates low polarity, co-solvent extraction with organic solvents can diversify the polarities of solvents thus giving more extraction selections.

In the early development of introducing SFE-CO_2 to extract compounds from mushroom, SFE-CO_2 was reported to be used in order to quickly and easily prepare samples from *A. bisporus* for profiling carboxylic and fatty acids [99].

Recently, most of the published studies investigated the different supercritical conditions (pressure, temperature and solvents) and also compared the results with those obtained from traditional extractions, such as Soxhlet and maceration (Table 7) [100, 101]. To evaluate the performance of extraction methods, antioxidant activities, chemical compositions (i.e., fatty acid) and extraction yields are studied on mushroom. SFE did not necessarily retain the highest desirable properties in the mushroom

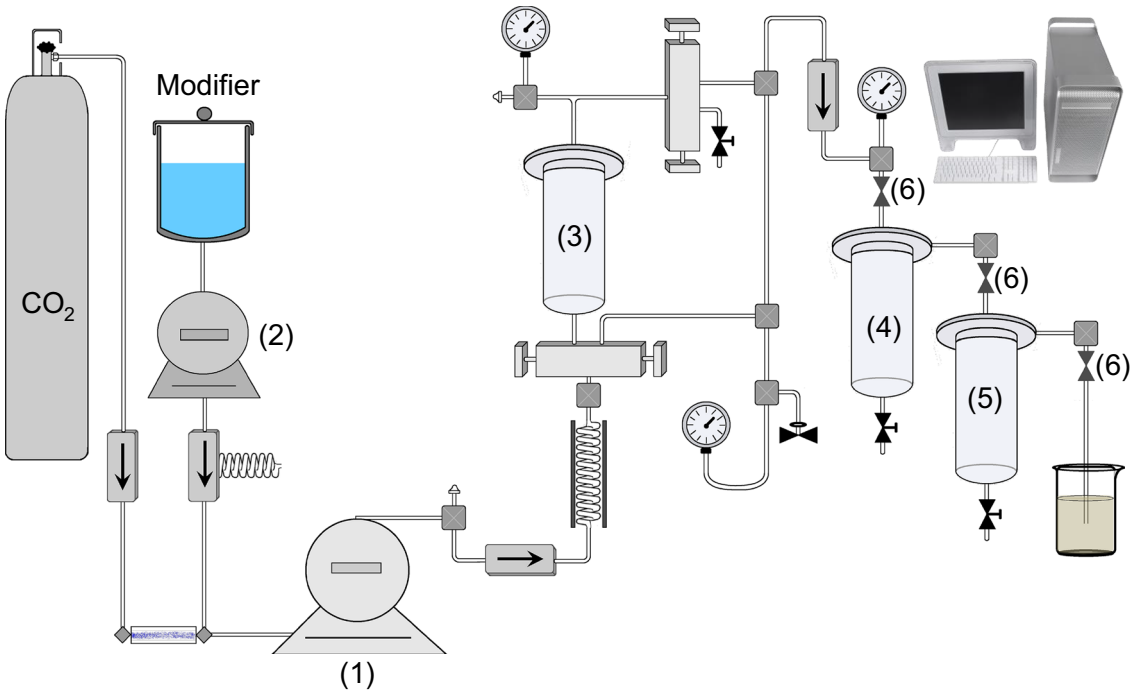

Fig. 5 SFE pilot plant apparatus. *1* CO_2 pump, *2* modifier pump, *3* extraction cell, *4* and *5* fractionation cells, *6* valve

extraction and traditional extractions (Soxhlet, ethanol, or ethyl acetate) showed better results (Table 7).

In addition, co-solvent SFE (ethanol-CO_2) could enhance hydrophilic antioxidants but reduce the yield of fatty acid because of the increase in polarity in the extraction fluid [101]. In another study, the effects of supercritical carbon dioxide extraction on the recovery of fatty acids from *B. edulis* mushroom were evaluated [96]. It was observed that fatty acid yields were augmented when pressure and extraction time increased. The authors also found a selective extraction of linoleic acid in the extracts obtained by supercritical carbon dioxide.

The prophylactic effect of CO_2, considered as an "inert" fluid for food processing, has often been reported in literature as one of the major benefits when it is used in its supercritical form, especially, when processing oxygen sensitive compounds. The application of supercritical CO_2 for such processes has been contrasted with the apparition of subcritical and supercritical water. This fluid, especially in its supercritical form, was applied in a wide range of applications, such as a medium for both organic [102] and inorganic [103] synthesis reactions, for the production of functional monomers from biomass [104], and for the conversion and destruction of either chemical wastes or toxic compounds [105].

SWE allows thus both extraction and reaction modes, when processing under specific conditions. However, although commonly considering CO_2 in both liquid and supercritical forms as unreactive media, it represents a potent catalytic medium, mainly due to the conducting hydrolytic-based reaction chemistry. Due to the presence of water in agricultural products, even in traces, this phenomenon is usually occurring, facilitating thus the equilibrium of carbonic acids [106] and a hydronium ion for acid-based catalysis.

The occurring reactions in subcritical water have been well described and reviewed in literature [107]. As reported, the role of subcritical and supercritical water depends on the type of application; it could therefore be used to alter selectively the composition of the extract, to obtain polymeric moiety and functional monomers from polymers, to enhance a polymerization reaction, or to produce mixtures for fermentation through depolymerized products degradation.

SWE and supercritical CO_2 are known to contribute and facilitate the formation of Maillard reaction products, as flavor precursors during food processing. Additionally, the hydrolysis in water of biopolymers leads to the generation of polyphenolic or flavonoid moieties, enhancing thus the food characteristics. For example, lignin could be treated using gas-expanded solvents to produce vanillin [108].

All of these phenomena occurring during the extraction of valuable compounds from agricultural products, depend on their thermal stability and the susceptibility of their conversion (e.g., polymer hydrolysis in aqueous media) to other products. Such competition is then occurring between the selective extraction process and its conversion to another compound by temperature and/or hydrolysis, even if the kinetics associated with the reaction are very slow or barely detectable. To describe this competitive situation, a model has been proposed by Duan [109], in which the time dependence of solute solid-phase concentration C_{Si} is given in the differential form by Eq. (10) [109].

$$\frac{dC_{Si}}{dt} = -k_{pi}a_p(m_iC_{Si} - C_{ti}) \tag{10}$$

Here, k_{pi} represents the solute mass transfer being extracted from the solid phase, a_p is the specific surface area of the solid, m_i represents the thermodynamic distribution coefficient, and C_{ti} is the solute concentration in the solid phase at time t. The differential equation describing the solute concentration mass balance C_{Li} as a function of time in the liquid phase is given by Eq. (11) [71].

$$\frac{dC_{Li}}{dt} = k_{pi}a_p\left(\frac{\rho_L}{\rho_S}\right)\frac{1}{F}(m_iC_{Si} - C_{Li}) - K_{Di}C_{Li} \tag{11}$$

where ρ_L and ρ_S represent the density of the liquid and solid phases, respectively. F represents the water to solid mass ratio, and K_{Di} is the constant of the degradation rate for the ith component.

In conclusion, SWE and SFE both present the possibility of clean chemical process to extract bioactive compounds from mushroom. Depending on characteristics of target compounds, researchers could change the solubility and polarity of extraction solvent by altering pressure, temperature, extraction solvent components, and extraction time.

Benefits and Limitations of Non-conventional Assisted Extraction Methodologies

Replacing the burdensome solvents (i.e., hexane, acetonitrile, methanol, dichloromethane, and toluene), used for long time in the extraction processes and the recovery of high-added value compounds, with green solvents such as CO_2, ethanol, and water is undoubtedly one of the challenges in both food and nutraceutical sector. Non-conventional methods are mainly devoted to such solvent replacement as well as the decrease in temperature and treatment time compared to conventional methods. Some of the technologies reviewed here are mature enough and already used at industrial scale (i.e., PEF); others (i.e., HVED) require more research developments, but, in any case, it is important that new steps be taken to help build a more rational use of our natural resources.

PEF treatment is one of the main non-conventional processes used in food and nutraceutical industries. The success of this process is related to its continuous operability associated with the very short treatment times. These features make it a suitable and an easy process to be adapted, in a sustainable way, to the integrated processes including pre-treatments, extractions, reactions, and transformations. By permeabilizing the cell membranes at relatively low temperatures, PEF treatment is a useful tool to protect thermolabile compounds from degradation. Furthermore, it is highly selective and allows the release of soluble intracellular matter, whereas application of solvents is needed for conventional methods, requiring further purification steps. Finally, PEF treatment increases the shelf life and preserves the product quality and freshness. However, the major concern for commercialization of PEF technology is the relatively high installation cost for industrial processes. Besides this point, the applicability of PEF process is highly dependent to the electrical conductivity of the treated product, making the process relatively complicated and requiring numerous pre-treatment processes (i.e., washing, centrifugation, etc.), especially for salty solutions. Furthermore, PEF technology showed limitations on solid and particulate food treatment and was mainly applied for pumpable foods.

The application of HVED is based on the phenomenon of electrical breakdown in water. Water vapor bubbles that are initially present in the solution or formed due to local heating are involved in this phenomenon and accelerate the process. HVED pre-treatment, causing even small cell damage, has shown high yield of extracted proteins from plant matrices, without quality degradation. This green extraction technique allows the recovery of nutritionally and high-added value compounds at low energy input compared to other non-conventional techniques (i.e., PEF, US, and MAE), as well as the reduction in the required diffusion temperature, the extraction time, and the amount of solvent. However, the HVED application for selective extraction of intracellular compounds showed limitations compared to PEF. Additionally, HVED treatment involves usually the fragmentation of the plant matrix and the release of small particles, requiring additional purification steps. Like PEF treatment, HVED presents applicability limitations with high solution's conductivity. Finally, up to now, no industrial scale application of HVED treatment was reported, requiring thus more deep researches.

UAE is an alternative affordable, effective, reproducible, simple and cheap method for the improved recovery of nutritionally valuable compounds (yields and kinetics) from different vegetal matters. This technique can be used alone and/or combined with conventional extraction method, and it requires low capital cost. Moreover, this methodology can reduce the temperature, thus being a potential alternative to preserve thermolabile compounds. In addition, can minimize solvent consumption, allowing the use of green solvents. However, one of the main limitations of UAE is that its effects are highly dependent of the matters and the presence of a disperse phase, which can promote the wave attenuation and thus reducing the effectiveness of this method.

On the other hand, MAE also allows improving the extraction yield of intracellular valuable compounds, decreasing the extraction time, and the solvent consumption compared to conventional methodologies. By contrast, the application of microwaves can have a negative impact in thermolabile compounds associated with microwave heating. Moreover, the polarity of compounds and solvent play an important role, thus difficulting the recovery of non-polar target compounds. In addition, the development of microwave equipment at large scale can require high investment costs.

The use of supercritical fluids for the extraction and recovery of high-added value compounds result as well in a "clean" extract when compared to other conventional extraction techniques. This technique leads obtaining highly purified extracts without residual organic solvents and interfering compounds extracted from the matrix. In spite of the potential of SFE technique, its usefulness could be related to the properties of the compound to be extracted from the matrix used. Furthermore, low polarity compounds are well extracted using SFE, considering especially the low polarity of supercritical CO_2. It is also notable that mild pressures and temperatures, lead obtaining volatile compounds without affecting their properties, allowing thus their direct analysis when coupled with chromatographic equipment. Usually, the most used techniques are gas chromatography (GC) or supercritical fluid chromatography (SFC). One of the limitations related to the use of SFE technique concerns that targeted polar compounds require conceiving other strategies for their extraction (i.e., using co-solvents). Moreover, the industrial applications are still limited by the high amounts of supercritical fluids required, which is in most of the cases being recycled.

Patents and Commercial Applications

Asian countries have been studying on extracting bioactive compounds from mushrooms for a long time. For example, in the Global Patent Search Network database (gpsn.uspto.gov), 6884 results from 1985 to 2012 released by the State Intellectual Property Office (SIPO) of the People's Republic of China were shown when searching with key word "mushroom extract". In comparison, there were only 138 results when searching the same key word within the US patent database (patft.uspto.gov) since 1976.

Traditionally, mushroom extract patents usually used hot water extraction, solvent extraction, dialysis, and gel

filtration to extract and purify bioactive compounds from mushrooms. Figure 6 illustrated the procedures of extracting dietary fiber, lentinan, and lentysine from Shiitake mushroom, adapted from [110]. The similar procedure was also described by others. For example, Zhuang et al. [111] obtained glycoprotein by soaking *Grifola frondosa* in hot water (100–120 °C) and ethanol before subjecting the resultant supernatant to dialysis. Similar extraction method was conducted to yield bioactive compounds with 100–2000 molecular weight from *A. blazei* Murill fruit bodies for suppressing breast cancer [112].

Using non-conventional methods to extract mushroom, however, was reported in only a few patents (Table 8) [113–115].

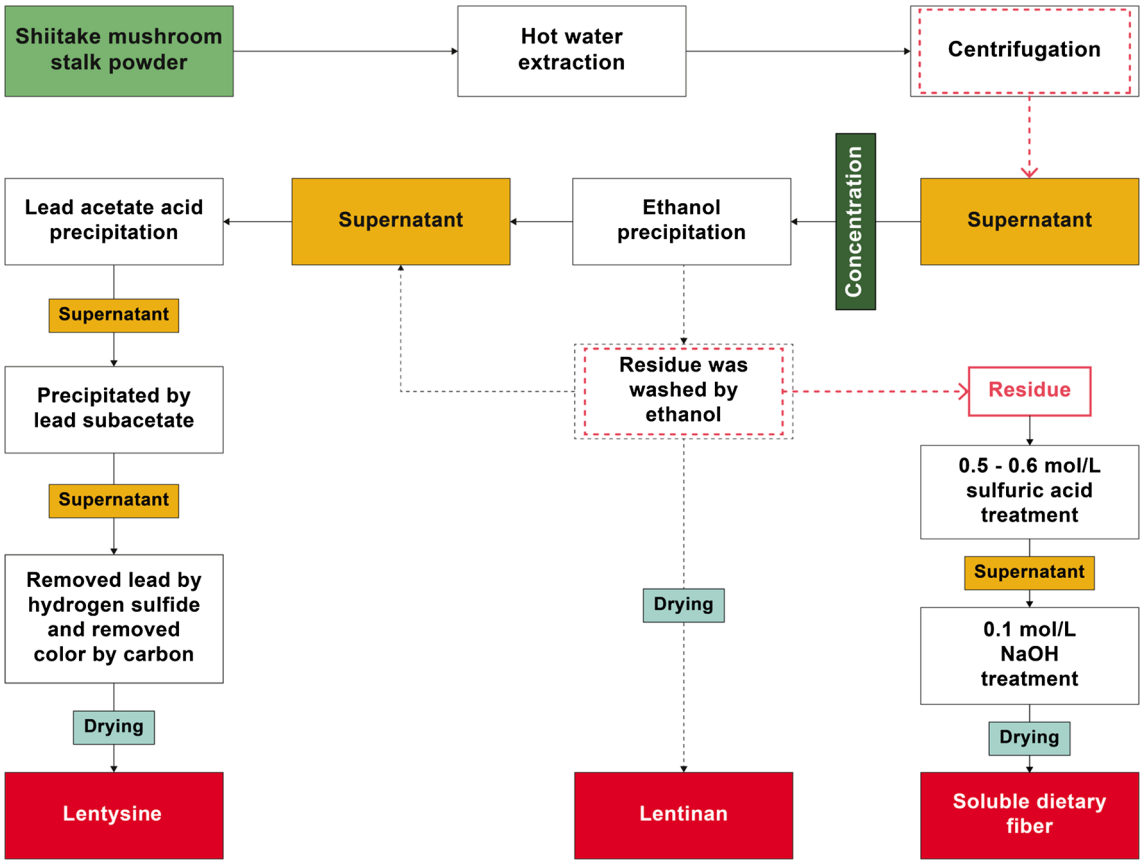

Fig. 6 Extraction diagram of lentysine, lentinan and dietary fiber from Shiitake mushroom (adapted from [110])

Table 8 Representative patents to non-conventional processes of mushroom

Mushroom variety	Processes	Compounds	Results	Patent no.	References
Portobello mushroom	Microwave-assisted extraction: 60–80 mesh of powder; 4–5 min extraction time; 1:10–1:100 solid–liquid ratio; and 200–800 W microwave power	Water-soluble polysaccharides (100–800 kDa) after purification	3–3.3 % w/w yield with more than 90 % purification	CN 103524636A	[113]
11 varieties of mushroom	Ionic liquid extraction: different percentages of ionic liquid [C_4mim]Cl to water (100 %:0–50 %:50 %) was used for extraction	Lentinan	0.03–0.05 % w/w yield	WO 2013140185A1	[114]
Ganoderma Lucidum (Lizhi mushroom) spores	SFE-CO_2: pressure 5–60 MPa; temperature 32–85 °C; extracting duration 0.5–6 h; carrier 85–100 % ethanol or water; flow rate 5–8 kg/h	Oleaginous substances	About 37 % w/w yield	US 6440420B1	[115]

Non-conventional methods claimed to have the advantage of replacing hot water and alkaline extractions while shortening the extraction time [114]. By employing supercritical fluid extraction, about 37 % w/w of oleaginous substances were yielded and the compounds were later proven to be of positive effects on improving skin conditions [113–115]. MAE extracted 3 % of 100–800 kDa polysaccharides from Portebella mushroom in 4–5 min [113]. In addition, ionic liquid extraction method was recently introduced to extract lentinan from 11 mushrooms, which was not found in any other publication yet [114].

Under CFR §21 (Code of Federal Regulations Title 21) in US Food and Drug Administration (FDA) database, only canned mushrooms are regulated. Regarding to fresh mushroom, Pennsylvania State University and the American Mushroom Institute developed Mushroom Good Agricultural Practice Programs to better guide mushroom growing, harvesting and shipping to meet food safety standards [116]. However, guideline of applying mushroom extract in food or nutraceutical products remains unclarified in the USA. On the other hand, Europe Commission categorizes mushrooms as novel food ingredients defined as "food ingredients that have not been used for human consumption to a significant degree in the EU before May 15, 1997." For example, in order to get approval under EU novel food category, Shiitake mushroom extract GlycaNovaTM was requested additionally substantial evidences to prove its safety for consumption as food ingredient [117]. The case to some extent indicates that the application of mushroom extracts as food ingredients in EU has more restriction rules.

Overall, most of the current patents use conventional extraction methods to extract bioactive compounds. Abundant patents have also proven the healthy effects of mushroom extracts. However, non-conventional extraction methods were only reported in several patents. In addition, regulation on mushroom and mushroom extracts in Western countries remains relatively unclear and under developed. More studies on toxicology of nutritionally valuable compounds from mushroom should be conducted.

Concluding Remarks

This review focuses on various technologies used for the extraction of bioactive compounds from mushrooms. Moreover, it provides a bird eye view on critical extraction parameters for maximum recovery of bioactive compounds. Overall, non-conventional cell disruption technologies may allow the extraction of nutritionally valuable compounds from mushrooms from an economical and environmental sustainable point of view. There is a need to develop a database to establish the optimum conditions to extract specific compounds with the appropriate technology and each mushroom family should be studied separately. Moreover, there is a need to study what compounds are better extracted and the nutritional quality of them. Some challenges must be addressed before non-conventional techniques become a reliable option for extractions, and they include production cost, scalability, and safety.

Acknowledgments The authors appreciate the support from the COST Action TD1104307 (EP4Bio2Med-European network for development of electroporation-based technologies and treatments).

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical Statement The manuscript represents a review article. All authors agree to its submission to Food Engineering Reviews and are responsible for the complete contents of their manuscript. All the authors guarantee that the manuscript, in its present or a substantially similar form, has not been published or is not being considered for publication elsewhere.

References

1. Uddin MN, Yesmin S, Khan MA et al (2011) Production of oyster mushrooms in different seasonal conditions of Bangladesh. J Sci Res 3:161–167
2. Commission USIT (2010) Mushrooms Publication ITS-07. Control no. 2010002
3. Barba FJ, Esteve MJ, Frígola A (2014) Bioactive components from leaf vegetable products. Stud Nat Prod Chem 41:321–346
4. Ajikumar PK, Tyo K, Carlsen S et al (2008) Terpenoids: opportunities for biosynthesis of natural product drugs using engineered microorganisms. Mol Pharm 5:167–190
5. Furlani RPZ, Godoy HT (2008) Vitamins B_1 and B_2 contents in cultivated mushrooms. Food Chem 106:816–819
6. Heleno SA, Barros L, Sousa MJ et al (2010) Tocopherols composition of Portuguese wild mushrooms with antioxidant capacity. Food Chem 119:1443–1450
7. Mattila P, Konko K, Eurola M et al (2001) Contents of vitamins, mineral elements, and some phenolic compounds in cultivated mushrooms. J Agric Food Chem 49:2343–2348
8. Tsai S-Y, Tsai H-L, Mau J-L (2008) Non-volatile taste components of *Agaricus blazei*, *Agrocybe cylindracea* and *Boletus edulis*. Food Chem 107:977–983
9. Mattila P, Salo-Valtonen P, Konko K et al (2002) Basic composition and amino acid contents of mushrooms cultivated in Finland. J Agric Food Chem 50:6419–6422
10. Dimou DM, Georgala A, Komaitis M, Aggelis G (2002) Mycelial fatty acid composition of *Pleurotus* spp. and its application in the intrageneric differentiation. Mycol Res 106:925–929
11. Pedneault K, Angers P, Gosselin A, Tweddell RJ (2006) Fatty acid composition of lipids from mushrooms belonging to the family Boletaceae. Mycol Res 110:1179–1183
12. Barros L, Baptista P, Correia DM et al (2007) Fatty acid and sugar compositions, and nutritional value of five wild edible mushrooms from Northeast Portugal. Food Chem 105:140–145

13. Reis FS, Barros L, Martins A, Ferreira ICFR (2012) Chemical composition and nutritional value of the most widely appreciated cultivated mushrooms: an inter-species comparative study. Food Chem Toxicol 50:191–197
14. Caglarirmak N (2011) Edible mushroom: as alternative food item. In: 7th international conference on mushroom biology and mushroom products, ICMBMP7, pp 548–554
15. Caglarirmak N (2011) Physical properties, nutrients and estimated volatiles of *Agaricus bisporus* (white) at two harvests. Ital J Food Sci 23:423–430
16. Esteve MJ, Farre R, Frigola A, Garcia-Cantabella JM (2001) Simultaneous determination of thiamin and riboflavin in mushrooms by liquid chromatography. J Agric Food Chem 49:1450–1454
17. Mataix-Verdu J (2003) Tabla de composición de los alimentos. Universidad de Granada, Granada
18. Caglarirmak N (2007) The nutrients of exotic mushrooms (*Lentinula edodes* and *Pleurotus species*) and an estimated approach to the volatile compounds. Food Chem 105:1188–1194
19. Hirasawa M, Shouji N, Neta T et al (1999) Three kinds of antibacterial substances from *Lentinus edodes* (Berk.) Sing. (Shiitake, an edible mushroom). Int J Antimicrob Agents 11:151–157
20. Mondal S, Chakraborty I, Pramanik M et al (2004) Structural studies of water-soluble polysaccharides of an edible mushroom, *Termitomyces eurhizus*. A reinvestigation. Carbohydr Res 339:1135–1140
21. Wei S, Van Griensven LJLD (2008) Pro- and antioxidative properties of medicinal mushroom extracts. Int J Med Mushrooms 10:315–324
22. Hu H, Zhang Z, Lei Z et al (2009) Comparative study of antioxidant activity and antiproliferative effect of hot water and ethanol extracts from the mushroom *Inonotus obliquus*. J Biosci Bioeng 107:42–48
23. Zheng W, Zhang M, Zhao Y et al (2011) Analysis of antioxidant metabolites by solvent extraction from sclerotia of *Inonotus obliquus* (Chaga). Phytochem Anal 22:95–102
24. Van Griensven LJLD, Shnyreva AV, Song W (2010) Extracts of medicinal mushrooms *Agaricus bisporus* and *Phellinus linteus* induce proapoptotic effects in the human leukemia cell line K562. Int J Med Mushrooms 12:167–175
25. Wang L, Weller CL (2006) Recent advances in extraction of nutraceuticals from plants. Trends Food Sci Technol 17:300–312
26. Adams DJ (2004) Fungal cell wall chitinases and glucanases. Microbiology 150:2029–2035
27. Enman J, Rova U, Berglund KA (2007) Quantification of the bioactive compound eritadenine in selected strains of shiitake mushroom (*Lentinus edodes*). J Agric Food Chem 55:1177–1180
28. Xu C, Tian Z, Zhang C et al (2014) Optimization of enzyme assisted extraction of polysaccharides from *Ganoderma lucidum*. Eng Sci 12:17–20
29. Chen J, Lai P, Shen H et al (2013) Effect of extraction methods on polysaccharide of *Clitocybe maxima* stipe. Adv J Food Sci Technol 5:370–373
30. Lebovka NI, Shynkaryk MV, El-Belghiti K et al (2007) Plasmolysis of sugarbeet: pulsed electric fields and thermal treatment. J Food Eng 80:639–644
31. Vorobiev E, Lebovka N (2010) Enhanced extraction from solid foods and biosuspensions by pulsed electrical energy. Food Eng Rev 2:95–108
32. Lebovka N, Vorobiev E, Chemat F (2011) Series: contemporary food engineering. CRC Press
33. Ade-Omowaye BIO, Rastogi NK, Angersbach A, Knorr D (2003) Combined effects of pulsed electric field pre-treatment and partial osmotic dehydration on air drying behaviour of red bell pepper. J Food Eng 60:89–98
34. Fincan M, DeVito F, Dejmek P (2004) Pulsed electric field treatment for solid–liquid extraction of red beetroot pigment. J Food Eng 64:381–388
35. Soliva-Fortuny R, Balasa A, Knorr D, Martín-Belloso O (2009) Effects of pulsed electric fields on bioactive compounds in foods: a review. Trends Food Sci Technol 20:544–556
36. Bluhm H, Sack M (2008) Electrotechnologies for extraction from food plants and biomaterials. Food engineering series. Springer, Berlin, pp 237–269
37. Boussetta N, Lesaint O, Vorobiev E (2013) A study of mechanisms involved during the extraction of polyphenols from grape seeds by pulsed electrical discharges. Innov Food Sci Emerg Technol 19:124–132
38. Boussetta N, Vorobiev E (2014) Extraction of valuable biocompounds assisted by high voltage electrical discharges: a review. Comptes Rendus Chim 17:197–203
39. Luengo E, Álvarez I, Raso J (2013) Improving the pressing extraction of polyphenols of orange peel by pulsed electric fields. Innov Food Sci Emerg Technol 17:79–84
40. Shynkaryk MV, Lebovka NI, Lanoisellé J-L et al (2009) Electrically-assisted extraction of bio-products using high pressure disruption of yeast cells (*Saccharomyces cerevisiae*). J Food Eng 92:189–195
41. Liu D, Lebovka NI, Vorobiev E (2011) Impact of electric pulse treatment on selective extraction of intracellular compounds from *Saccharomyces cerevisiae* yeasts. Food Bioprocess Technol 6:576–584
42. Grimi N, Dubois A, Marchal L et al (2014) Selective extraction from microalgae *Nannochloropsis* sp. using different methods of cell disruption. Bioresour Technol 153:254–259
43. Tsong TY (1992) Time sequence of molecular events in electroporation. In: Chand DC, Chassy BM, Saunders JA, Sowers AE (eds) Guide electroporation electrofusion. Academic Press, New York, pp 47–62
44. Kotnik T, Miklavčič D, Slivnik T (1998) Time course of transmembrane voltage induced by time-varying electric fields—a method for theoretical analysis and its application. Bioelectrochem Bioenerg 45:3–16
45. Kinosita K, Hibino M, Itoh H et al (1992) Events of membrane electroporation visualized on a time scale from microsecond to seconds. In: Chang DC, Chassy BM, Saunders JA, Sowers AE (eds) Guide electroporation electrofusion. Academic Press, New York, pp 29–46
46. Lebedeva VE (1987) Electric breakdown of bilayer lipid membranes at short times of voltage effect. Biol Membr 4:994–998
47. Rogov IA, Adamenko VY, Nekrutman SV et al (1981) Electrophysical, optical and acoustical properties of foods. Legkaya i Pishchevaya Promyshlennost, Moscow
48. DeBruin KA, Krassowska W (1999) Modeling electroporation in a single cell. I. Effects of field strength and rest potential. Biophys J 77:1213–1224
49. Angersbach A, Heinz V, Knorr D (1999) Electrophysiological model of intact and processed plant tissues: cell disintegration criteria. Biotechnol Prog 15:753–762
50. Barba FJ, Puértolas E, Brnčić M et al (2015) Emerging extraction. In: Galanakis CM (ed) Food waste recovery: processing technologies and industrial techniques. Academic Press, London, pp 249–272
51. Puértolas E, Luengo E, Álvarez I, Raso J (2012) Improving mass transfer to soften tissues by pulsed electric fields: fundamentals and applications. Annu Rev Food Sci Technol 3:263–282
52. Zhang T-H, Wang S-J, Liu D-R et al (2011) Optimization of exopolysaccharide extraction process from Tibetan spiritual

mushroom by pulsed electric fields. J Jilin Univ Eng Technol Ed 41:882–886
53. Li C, Mao X, Xu B (2013) Pulsed electric field extraction enhanced anti-coagulant effect of fungal polysaccharide from Jew's ear (*Auricularia auricula*). Phytochem Anal 24:36–40
54. Parniakov O, Lebovka NI, Van Hecke E, Vorobiev E (2014) Pulsed electric field assisted pressure extraction and solvent extraction from mushroom (*Agaricus bisporus*). Food Bioprocess Technol 7:174–183
55. Herrero M, Cifuentes A, Ibañez E (2006) Sub- and supercritical fluid extraction of functional ingredients from different natural sources: plants, food-by-products, algae and microalgae: a review. Food Chem 98:136–148
56. Roselló-Soto E, Galanakis CM, Brnčić M et al (2015) Clean recovery of antioxidant compounds from plant foods, by-products and algae assisted by ultrasounds processing. Modeling approaches to optimize processing conditions. Trends Food Sci Technol 42:134–149
57. Soria AC, Villamiel M (2010) Effect of ultrasound on the technological properties and bioactivity of food: a review. Trends Food Sci Technol 21:323–331
58. Deng Q, Zinoviadou KG, Galanakis CM et al (2014) The effects of conventional and non-conventional processing on glucosinolates and its derived forms, isothiocyanates: extraction, degradation, and applications. Food Eng Rev 7:357–381
59. Barba FJ, Grimi N, Vorobiev E (2014) New approaches for the use of non-conventional cell disruption technologies to extract potential food additives and nutraceuticals from microalgae. Food Eng Rev 7:45–62
60. Zheng Y, Li Y, Wang W-D (2014) Optimization of ultrasonic-assisted extraction and in vitro antioxidant activities of polysaccharides from *Trametes orientalis*. Carbohydr Polym 111:315–323
61. You Q, Yin X, Ji C (2014) Pulsed counter-current ultrasound-assisted extraction and characterization of polysaccharides from *Boletus edulis*. Carbohydr Polym 101:379–385
62. Cheung Y-C, Siu K-C, Wu J-Y (2013) Kinetic models for ultrasound-assisted extraction of water-soluble components and polysaccharides from medicinal fungi. Food Bioprocess Technol 6:2659–2665
63. Cheung Y-C, Wu J-Y (2013) Kinetic models and process parameters for ultrasound-assisted extraction of water-soluble components and polysaccharides from a medicinal fungus. Biochem Eng J 79:214–220
64. Wang T, Liang H, Yuan Q (2011) Optimization of ultrasonic-stimulated solvent extraction of sinigrin from Indian mustard seed (*Brassica Juncea* L.) using response surface methodology. Phytochem Anal 22:205–213
65. Ma J, Qiao Z, Xiang X (2011) Optimisation of extraction procedure for black fungus polysaccharides and effect of the polysaccharides on blood lipid and myocardium antioxidant enzymes activities. Carbohydr Polym 84:1061–1068
66. Tian Y, Zeng H, Xu Z et al (2012) Ultrasonic-assisted extraction and antioxidant activity of polysaccharides recovered from white button mushroom (*Agaricus bisporus*). Carbohydr Polym 88:522–529
67. Zou Y, Xie C, Fan G et al (2010) Optimization of ultrasound-assisted extraction of melanin from *Auricularia auricula* fruit bodies. Innov Food Sci Emerg Technol 11:611–615
68. Petrović J, Papandreou M, Glamočlija J et al (2014) Different extraction methodologies and their influence on the bioactivity of the wild edible mushroom *Laetiporus sulphureus* (Bull.) Murrill. Food Funct 5:2948–2960
69. Lebovka NI, Vorobiev E, Chémat F (2012) Enhancing extraction processes in the food industry. CRC Press, Boca Raton
70. Kingston HM, Haswell SJ (1997) Microwave-enhanced chemistry: fundamentals, sample preparation, and applications. American Chemical Society, Washington
71. Proctor A (2010) Alternatives to conventional food processing. Springer, New York
72. Chan C-H, Yusoff R, Ngoh G-C, Kung FWL (2011) Microwave-assisted extractions of active ingredients from plants. J Chromatogr A 1218:6213–6225
73. Mandal V, Yogesh-Mohan SH (2007) Microwave assisted extraction: an innovative and promising extraction tool for medicinal plant research. Pharmacogn Rev 1:7–18
74. Ma Y-A, Cheng Y-M, Huang J-W et al (2014) Effects of ultrasonic and microwave pretreatments on lipid extraction of microalgae. Bioprocess Biosyst Eng 37:1543–1549
75. Özyürek M, Bener M, Güçlü K, Apak R (2014) Antioxidant/antiradical properties of microwave-assisted extracts of three wild edible mushrooms. Food Chem 157:323–331
76. Young JC (1995) Microwave-assisted extraction of the fungal metabolite ergosterol and total fatty acids. J Agric Food Chem 43:2904–2910
77. Zhang Z, Lv G, Pan H et al (2011) Optimization of the microwave-assisted extraction process for polysaccharides in himematsutake (*Agaricus blazei* Murrill) and evaluation of their antioxidant activities. Food Sci Technol Res 17:461–470
78. Song J-F, Li D-J, Liu C-Q (2009) Response surface analysis of microwave-assisted extraction of polysaccharides from cultured *Cordyceps militaris*. J Chem Technol Biotechnol 84:1669–1673
79. Ru QM, Zhang LR, Chen JD et al (2009) Microwave-assisted extraction and identification of polysaccharide from *Lycoris aurea*. Chem Nat Compd 45:474–477
80. Dong J-Z, Wang Z-C, Wang Y (2011) Rapid extraction of polysaccharides from fruits of *Lycium barbarum* L. J Food Biochem 35:1047–1057
81. Huang S-Q, Ning Z-X (2010) Extraction of polysaccharide from *Ganoderma lucidum* and its immune enhancement activity. Int J Biol Macromol 47:336–341
82. Chen Y, Gu X, Huang S-Q et al (2010) Optimization of ultrasonic/microwave assisted extraction (UMAE) of polysaccharides from *Inonotus obliquus* and evaluation of its anti-tumor activities. Int J Biol Macromol 46:429–435
83. Wang H, Zhao Q, Song W et al (2011) High-throughput dynamic microwave-assisted extraction on-line coupled with solid-phase extraction for analysis of nicotine in mushroom. Talanta 85:743–748
84. Dörnte B, Kües U (2013) Fast microwave-based DNA extraction from vegetative Mycelium and fruiting body tissues of Agaricomycetes for PCR amplification. Curr Trends Biotechnol Pharm 7:825–836
85. Galanakis CM, Barba FJ, Prasad KN (2015) Cost and safety issues of emerging technologies against conventional techniques. In: Galanakis CM (ed) Food waste recovery: processing technology and industrial techniques, 1st edn. Elsevier–Academic Press, London, pp 323–338
86. Golmakani M-T, Rezaei K (2008) Comparison of microwave-assisted hydrodistillation with the traditional hydrodistillation method in the extraction of essential oils from *Thymus vulgaris* L. Food Chem 109:925–930
87. Luque De Castro MD, Jiménez-Carmona MM, Fernández-Pérez V (1999) Towards more rational techniques for the isolation of valuable essential oils from plants. TrAC Trends Anal Chem 18:708–716
88. Smith RM (2006) Superheated water: the ultimate green solvent for separation science. Anal Bioanal Chem 385:419–421
89. Askin R, Sasaki M, Goto M (2010) Recovery of water-soluble compounds from *Ganoderma lucidum* by hydrothermal treatment. Food Bioprod Process 88:291–297

90. Jo E-K, Heo D-J, Kim J-H et al (2013) The effects of subcritical water treatment on antioxidant activity of golden oyster mushroom. Food Bioprocess Technol 6:2555–2561
91. Seo H-K, Lee S-C (2010) Antioxidant activity of subcritical water extracts from chaga mushroom (*Inonotus obliquus*). Sep Sci Technol 45:198–203
92. Yang L, Qu H, Mao G et al (2013) Optimization of subcritical water extraction of polysaccharides from *Grifola frondosa* using response surface methodology. Pharmacogn Mag 9:120–129
93. Matsunaga Y, Wahyudiono Machmudah S et al (2014) Hot compressed water extraction of polysaccharides from *Ganoderma lucidum* using a semibatch reactor. Asia-Pac J Chem Eng 9:125–133
94. Ozel MZ, Kaymaz H (2004) Superheated water extraction, steam distillation and Soxhlet extraction of essential oils of *Origanum onites*. Anal Bioanal Chem 379:1127–1133
95. Lo TCT, Hsin HT, Ai YW, Chang CA (2007) Pressurized water extraction of polysaccharides as secondary metabolites from *Lentinula edodes*. J Agric Food Chem 55:4196–4201
96. Vidovic S, Mujic I, Zekovic Z et al (2011) Extraction of fatty acids from *Boletus edulis* by subcritical and supercritical carbon dioxide. JAOCS J Am Oil Chem Soc 88:1189–1196
97. Goto M, Sato M, Hirose T (1993) Extraction of peppermint oil by supercritical carbon dioxide. J Chem Eng Jpn 26:401–407
98. Mhemdi H, Rodier E, Kechaou N, Fages J (2011) A supercritical tuneable process for the selective extraction of fats and essential oil from coriander seeds. J Food Eng 105:609–616
99. Abdullah MI, Young JC, Games DE (1994) Supercritical fluid extraction of carboxylic and fatty acids from *Agaricus* spp. mushrooms. J Agric Food Chem 42:718–722
100. Kitzberger CSG, Smânia A Jr, Pedrosa RC, Ferreira SRS (2007) Antioxidant and antimicrobial activities of shiitake (*Lentinula edodes*) extracts obtained by organic solvents and supercritical fluids. J Food Eng 80:631–638
101. Mazzutti S, Ferreira SRS, Riehl CAS et al (2012) Supercritical fluid extraction of *Agaricus brasiliensis*: antioxidant and antimicrobial activities. J Supercrit Fluids 70:48–56
102. Rayner CM (2007) The potential of carbon dioxide in synthetic organic chemistry. Org Process Res Dev 11:121–132
103. Savage PE, Gopalan S, Mizan TI et al (1995) Reactions at supercritical conditions: applications and fundamentals. AIChE J 41:1723–1778
104. Sasaki M, Fang Z, Fukushima Y et al (2000) Dissolution and hydrolysis of cellulose in subcritical and supercritical water. Ind Eng Chem Res 39:2883–2890
105. Abeln J, Kluth M, Petrich G, Schmieder H (2001) Supercritical water oxidation (SCWO): a process for the treatment of industrial waste effluents. High Press Res 20:537–547
106. Hunter SE, Savage PE (2008) Quantifying rate enhancements for acid catalysis in CO_2-enriched high-temperature water. AIChE J 54:516–528
107. Liotta CL, Hallett JP, Pollet P, Eckert CA (2007) Reactions in nearcritical water. In: Lindström U (ed) Organic reactions in water. Blackwell, Oxford, pp 256–300
108. Eckert C, Liotta C, Ragauskas A et al (2007) Tunable solvents for fine chemicals from the biorefinery. Green Chem 9:545–548
109. Duan L (2005) Extraction of silymarins from milk thistle, *Silybum marianum*, using hot water as solvent. University of Arkansas, USA
110. Yang Y, Tang M, Dong W (2010) Extraction method of lentinan, eritadenine and mushroom dietary fiber. Patent CN102199223A
111. Zhuang C, Kawagishi H, Preuss HG (2007) A glycoprotein with antidiabetic, antihypertensive, antiobesity and antihyperlipidemic effects from *Grifola frondosa*, and a method for preparing same. Patent CA2455655C
112. Lee I (2011) Extract from *Agaricus blazei* Murill capable of suppressing breast cancer. US8034386 B2
113. Zhang Y, Jie J, Zhang M, Ma G (2013) Preparation method for Portobello mushroom polysaccharide. CN103524636A
114. Earle M, Gilea M Lentinan extraction process from mushrooms using ionic liquid. WO2013140185A1
115. Liu X, Huang XN, Chung PCK (2002) Method for extracting oleaginous substances from germination-activated *Ganoderma lucidum* spores. US6440420B1
116. MGAP (2010) The mushroom good agricultural practices. http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5095445
117. Starling S (2008) Mushroom extract seeks Novel Foods approval. Nutraingredients, July 7, 2008. http://www.nutraingredients.com/Regulation-Policy/Mushroom-extract-seeks-Novel-Foods-approval-again. Accessed Oct 6, 2015