Chapter 13
Innovative Technologies Used at Pilot Plant and Industrial Scales in Water-Extraction Processes

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Abstract Water remains the cheapest and the safest solvent to eco-friendly extract number of biogenic substances from the worldwide biodiversity to produce natural water-soluble extracts containing several biomolecule families such as polysaccharides, proteins, polyphenols, glycosides, etc. Among these water-soluble compounds, some showed potential free-radical scavenging capacity and antioxidant activity. As extraction processes were often time consuming, mechanical operations can be added to the extraction process to speed up water diffusion of valuable compounds from raw material. Apart from using conventional operating techniques such as mechanical stirring coupled with extraction medium heating, newly developed ones may increase efficiency of water-extraction processing. These innovative techniques include ultrasound-assisted extraction, pressurised hot water extraction, negative pressure cavitation-assisted extraction and pulsed electric field-assisted extraction. Some of these techniques are still under development at various scales, from the laboratory to the pilot plant, but others are already operational and used in industrial processes. After water-extraction step, purification and concentration of extracted products is often needed. Additional process steps are added, including membrane separation technology and gel column chromatography. They are already used at industrial scales and are preferred to heat-based separation techniques. They are claimed to better preserve biological activity of most of the heat-sensitive water-extracted compounds as they efficiently operate and avoid compound liquid–gas phase transition. They remain among the most energy-saving technological

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systems and are frequently called ‘green technologies’. In this chapter, some of these innovative technologies involved in water-extraction processes are presented, and when applicable, pilot plant- or industrial-scale applications are described.

Green technologies aim to preserve the quality of the environment and the rational utilisation of natural resources when they are used in transformation processes of vegetal raw materials. To implement these objectives in practice, they are used to prevent or to minimise the negative impact that some extraction processes may have on the surrounding environment. They encourage the development of extraction procedures that avoid, or reduce as far as possible, using extraction medium made of hazardous substances or that produce new pollutants and waste.

To adapt the general principles of the green chemistry to plant extraction processing, a similar approach has to be extended to the development of technologies associated in the extraction processes, leading to the production of new added-value natural water extracts obtained from various sources of vegetal raw material. These principles are as follows:

1. To substitute the use of dangerous organic solvents with number of less hazardous alternatives
2. To encourage the use of emerging extraction technologies
3. To make maximum use of high-efficiency separation techniques involving less toxic organic solvents or using only products that are least harmful for the environment

Solid–liquid extraction is a separation process involving transfer of solutes from a solid matrix into a liquid, named solvent. Water is recognised as the most ‘green’ solvent because it is non-flammable, non-toxic, readily available and eco-friendly compatible with the environment. Because of the polarity of water, many hydrophilic compounds such as polyphenols, protein, glycosides, polysaccharides, etc., can be easily dissolved in water.

The traditional water-extraction techniques commonly used at laboratory level or industrial scale include maceration with or without stirring, mild heating or heating under reflux. These techniques require generally long extraction times and large amounts of sample and water. Especially, the heating process may destroy the thermal-sensitive compounds which are normally bioactive ones.

To improve efficiency of water extraction, several innovative technologies have been developed. Among them, the most popular and technologically advanced are ultrasound-assisted extraction, pressurised hot water extraction, negative pressure cavitation-assisted extraction and pulsed electric field-assisted extraction. Some of them are still under development at various scales, but the others are already involved in industrial processes.

Depending on the technological water-extraction process applied, additional steps may be needed such as purification and concentration of the compounds extracted in the aqueous solvent. Membrane separation technology and gel column chromatography are already used at these process steps. They are preferred to

the classical heat-based separation/concentration techniques because they better preserve most part of the biological activity of the heat-sensitive extracted compounds, as they can also operate efficiently at room temperature. They remain among the most energy-saving technologies; this is why they are frequently classified as 'green technologies'.

Some of these innovative technologies involved in water-extraction processes will be described in this chapter, and some applications at industrial and pilot plant scales will be also presented.

13.1 Ultrasound-Assisted Water Extraction (UAWE)

Extraction of bioactive compounds using ultrasound (US) is one of the upcoming extraction techniques that can offer high operation reproducibility with short extraction times, simplified manipulation, reduced solvent consumption, low-temperature uses and reduced energy usage.

Ultrasounds are mechanic waves that necessitate an elastic medium to spread over. The difference between sounds and ultrasounds is the frequency of the wave of the signal: ultrasounds can be defined as vibrations of the same kind as 'normal' sound but of such a high frequency (higher than 20 kHz) that they cannot be heard by the human ear. The field of the ultrasounds is limited in the upper frequencies by those of the microwaves, starting at a frequency around 10 MHz.

As a sound wave passes through an elastic medium such as water, it induces a longitudinal displacement of particles, as if the source of the sound wave acted as a piston on the surface of this medium [1]. This action generates successive compression and decompression cycles within the medium. If cycles follow each other rapidly in a high frequency, small gas or vapour bubbles are formed, developed and collapsed almost immediately and violently within the medium. This phenomenon, called cavitation, created locally very intense physical or chemical effects, as a result of extreme conditions of temperature and pressure produced when the cavitation bubbles implodes. The temperature and the pressure have been estimated to be up to 5,000 K and 2,000 atm in an ultrasonic bath at room temperature, which can lead to the disruption of biological membranes placed in this water bath, making easier mass transfers by increasing diffusion of water-soluble compounds of the material into the water and by enhancing water penetration into the cellular material. Carla Da Porto et al. [2] have compared the efficiency of the ultrasound-assisted extraction (UAE) with conventional extraction applied to plant material. They showed that 15 min treatment grape samples using UAE lead to the same amounts of total polyphenols and total tannins than water maceration of the sample during 12 h. The published work of Corrales [3] showed also that total phenolic content obtained after 1 h time water UAE of a grape sample was 50 % higher than the one obtained using classical water maceration. Antioxidant activity of the ultrasound-assisted extract was about twofold higher than those of the extract obtained by maceration.

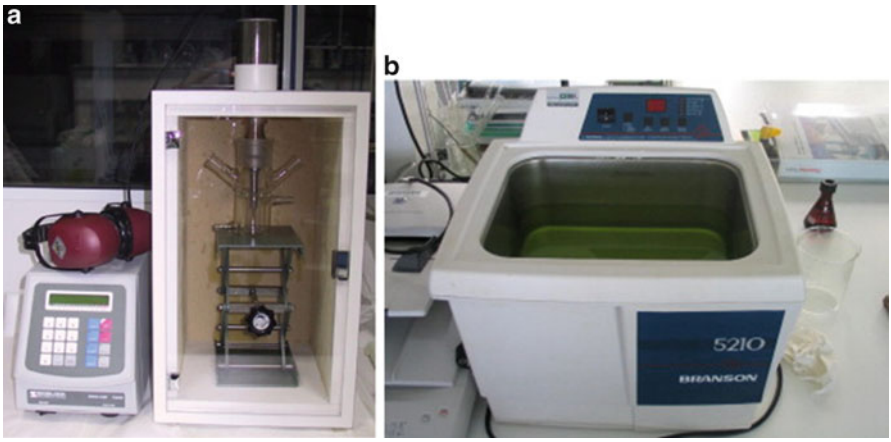

Fig. 13.1 Independent US probe (**a**) and built-in US water bath (**b**) for laboratory-scale uses (Reprint from [1] with permission from Elsevier)

13.1.1 Characteristic Parameters of UAWE

The specific parameters used to describe an UAWE procedure are (1) the frequency, (2) the power and (3) the ultrasonic intensity of the ultrasounds used.

The frequency of the ultrasounds is currently included in the range of 15 kHz to 60 kHz. Usually, only the 20–25 kHz frequency range is used for ordinary extractions, cleaning or degassing operations. Ultrasound power applied is generally less than 500 W for a laboratory-scale extraction apparatus and can be within 1–3 kW for pilot plant- or industrial-scale systems [4].

The ultrasonic intensity (UI) generated by an ultrasound probe in a cylindrical reactor tank is calculated from the following equation:

$$\mathrm{UI} = \frac{4P}{\pi D^2} \tag{13.1}$$

where UI ($\mathrm{W \cdot cm^{-2}}$) is the ultrasonic intensity, P (W) is the ultrasound power and D (cm) is the internal diameter of the reactor tank.

13.1.2 Laboratory- and Industrial-Scale UAWE Apparatus

Ultrasound-assisted extraction is also called sonication or ultrasonication. At the laboratory level, it is usually applied using an ultrasonic probe (Fig. 13.1a) or an ultrasonic bath (Fig. 13.1b). For the ultrasonic probe system, sonication is generally made using a single ultrasonic probe equipped with its electronic regulation. The

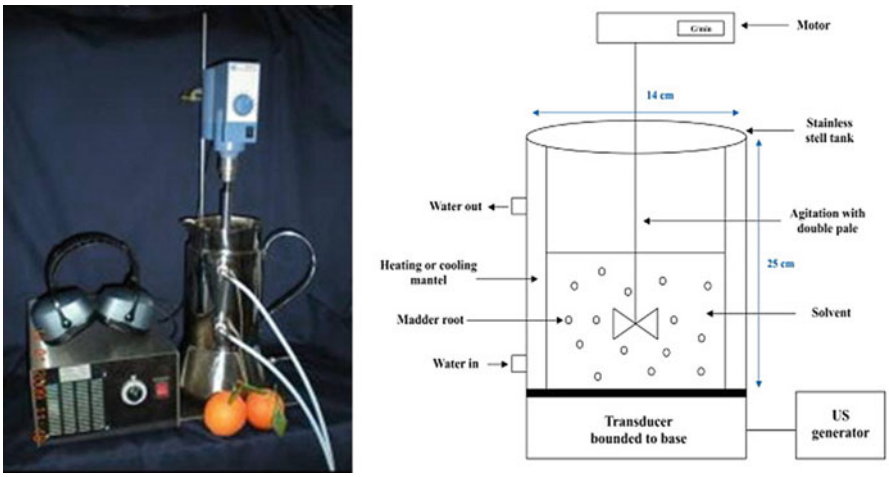

Fig. 13.2 Laboratory-scale UAWE reactor with controlled temperature and stirring-speed (Reprint from [1] with permission from Elsevier)

probe is immersed in a beaker where the material is soaked in solvent. The ultrasonic frequency can be regulated of some models and the ultrasonic intensity is delivered on a small surface (only the tip of the probe) which is more powerful than the ultrasonic bath. This system of probe is widely used for sonication of small volumes of sample, but it causes a temperature rise significantly. The US bath is more frequently found in laboratories and used as an all-purpose extraction or cleaning apparatus. The US frequency cannot be adjusted manually and the delivered intensity is low and often highly attenuated by the water volume used or by some adapted operating conditions to the sample quantity available. When the sample quantity of the material to be extracted is small, it is a common practice to dip the small sample into the water contained by a small beaker, which in turn placed into the liquid of the water bath.

A more sophisticated laboratory-scale UAE reactor was developed by REUS Co (www.etsreus.com, FRANCE), as shown in Fig. 13.2. This reactor can be used to study UAE of different types of samples, under various controlled operating conditions. This apparatus can be used to perform preliminary extraction experiments for new applications of UAE of material samples. It helps to determine the best extraction conditions in view to scale up the operation and to develop new extraction process to operate at a higher scale using pilot plant- or industrial-scale UAE extractors. This laboratory-scale apparatus consists of a double-walled bowl (0.5–3 L) made of stainless steel that allows the thermoregulation of the extraction medium. The bowl stands on base which contained the ultrasonic probes which is controlled by an external electronic regulation. The ultrasonic intensity delivered is about 1 W/cm^2 with a constant frequency of 25 kHz. A mobile stirring device is added to the system and is composed of a propeller moved by a variable speed

Fig. 13.3 Industrial-sale UAWE equipments with 50, 500, and 1,000 L reactor tank capacities (Reprint from [1] with permission from Elsevier)

electric motor. The stirring system can be adjusted in direction of rotation and speed, and the propeller can be set at the required depth in the extraction medium.

To run out pilot plant- and industrial-scale trials or to scale up UAE from laboratory experiments, REUS offers UAE reactors with a tank capacity ranging from 30 to 1,000 L (Fig. 13.3). A pump system is adapted to the ultrasonic tank in order to fill it at the start of the operation. The pumping system can also be used, to stir the extraction medium by continuous feeding back the tank with the water-sample mixture collected at the bottom of the tank. It is also used at the end of the UAE operation to empty the tank.

Industrial-scale UAWE equipments are generally preferred to conduct extraction operations in a continuous countercurrent flow mode which is a more suitable mode at this level. For this reason, an industrial extractor, using a counterflow extractor assisted by a sound transduction system, was invented by Pacheco et al. [5]. According to the description given in the patent, the equipment (Fig. 13.4) included an inclined casing (12) containing a helical screw conveyor (13) equipped with lots of blades (17), a hopper (21) used to feed the extractor with the raw material at the lower end of the casing (15). A second helical screw conveyor (22) forming a specific angle θ with the axis of the main screw of the casing allowed to continuously load the raw material in the extractor. An outlet hopper was located at the upper end

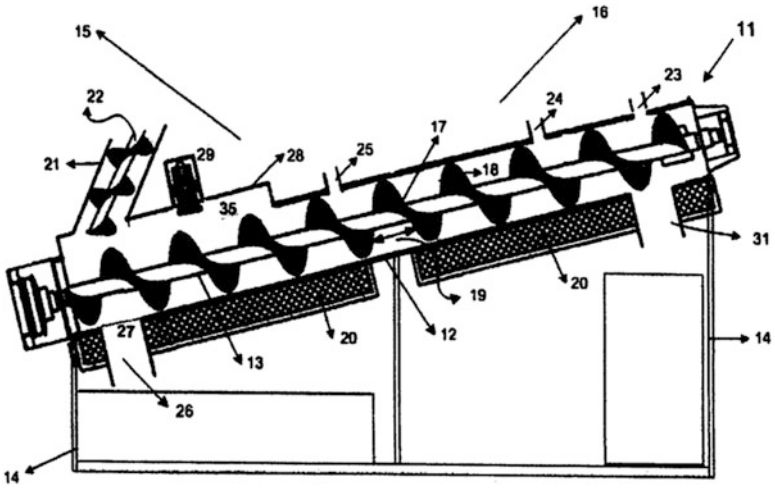

Fig. 13.4 Schematic diagram of the ultrasound-assisted countercurrent flow extractor (According to [5])

(31) of the casing to release the extracted material. The equipment was completed with a water load line (16) with different water upper inlets (23, 24, 25) to fill the casing with water for material extraction which was recovered with the extracted water-soluble compounds from the bottom outlets (19, 20). Two discharge lines (27, 31) were placed at the front and the end of the casing to continuously recover the extracted material during the process and to empty the casing at the end of the operation. The extracted material was collected into two boxes (14, 26). During the extraction, liquid and solid media were separated through a built-in filter (20). The US transducer (29) is located at the lower end (15) of the casing, close to the material feeder to provide ultrasounds as soon as the material entered the casing and put into contact with extraction water.

Based on the principle of this invention, many small Chinese factories produced similar equipments for industrial continuous countercurrent flow extraction (Fig. 13.5). According to the production levels targeted by the factories, various sizes of such equipments were built to process from 33 to 1,350 kg/h of raw material (Sinobest, www.sinobest.com.cn; Jining Tianyu www.tychaosheng.com). Some of these extractors can operate using at the same time two different levels of ultrasonic frequency: 20 kHz are first applied at the casing entrance (material feeding section) and 45 kHz are then applied around the upper casing outlet (material discharge section). The relative low ultrasonic frequency favours initiation of rapidly formation and growing cavitation bubbles, and the high frequency allows a better compound diffusion between the raw plant material and the extraction water [6, 7].

Fig. 13.5 A general view of a dynamic countercurrent UAWE Chinese plant

13.1.3 Application of UAWE at Pilot Plant and Industrial Scales

Ultrasound-assisted water extraction (UAWE) is still considered as an emerging technology that begins to have several new applications in the sector of the food and pharmaceutical industries [7]. After laboratory-scale feasibility and reproducibility studies have been undertaken, pilot plant experiments in batch mode have been tested and validated, using pre-industrial equipments. Optimisation of operation parameters of the process, conducted in a semi-continuous mode, was completed. Up-scaling was then made to validate the process development at an industrial scale and in a continuous production mode.

Several teams of French researchers [1, 8–10] proceeded to such UAWE developments, in accordance with the principles stated by the green chemistry. They applied this green technology to apple pomace processing, a waste from the apple juice and cider manufacturing processes. This waste contained polyphenol molecules showing antioxidant properties [9]. The studies were first performed using a laboratory-scale ultrasound-assisted extractor (PEX1, R.E.U.S., Contes, France), equipped with a 1 L volume beaker (i.d. = 14 cm, 10 cm height). The ultrasonic probe delivered a 25 kHz ultrasound frequency and a 150 W power. The UAWE parameters (ultrasonic intensity, temperature and sonication duration) were optimised using a central composite design within the following parameter ranges: 0.335–0.764 $W \cdot cm^{-2}$ for ultrasonic intensity and 10–40 °C for temperature and 5–55 min for sonication time. The extraction medium used was a 50 mM malate buffer solution at pH = 3.8. The best extraction conditions were found: 0.764 $W \cdot cm^{-2}$ for

Fig. 13.6 Pilot plant-scale model of 30 L volume UAWE apparatus: general view, inside of the reactor tank, recirculating pump and outside bottom of the reactor, top of the reactor with opened protection door (Reprint from [11] with permission from Elsevier)

ultrasound intensity, 40 °C for temperature and 40 min for extraction time. The solid–liquid ratio was optimised as 150 $g \cdot L^{-1}$ dry material/water in function of total polyphenols obtained by a conventional maceration method.

The optimised UAWE lead to a total amount of extracted polyphenol compounds 30 % higher (555 mg of catechin equivalent per 100 g of dry pomace weight) than the one obtained by the conventional extraction, simple water maceration.

Then, the first scaling-up study is undertaken at pilot plant scale, using an ultrasound-assisted extractor equipped with a 30 L volume extraction tank and four probes delivering a ultrasonic frequency of 25 kHz with a total power of 4×200 W (Fig. 13.6). The polyphenol extraction yield was about the same level as those obtained by the extraction trial run at the lab scale using the optimised experimental conditions. The extraction was completed within 40 min time, and the total polyphenol of the water extract obtained was 560 mg catechin equivalent per 100 g of dry pomace weight.

13.2 Microwave-Assisted Extraction (MAE)

Microwaves are non-ionising electromagnetic waves that combine the use of an electric field and of a magnetic field, each one oscillating in a perpendicular plane to the other at a frequency range of 0.3–300 GHz. Microwaves are characterised by the three properties: transmittance, reflectance and absorption. Microwaves almost go through materials such as glass, plastic or porcelain or even some organic liquid without being absorbed (transmittance is total). However, metallic material can totally reflect microwaves (reflectance is total), but liquid media, such as water or polar molecule solutions, can absorb microwaves to a certain extent, resulting in heat production within the media.

Considering that water molecules are known as dipoles, a sort of bar magnet, with a positive and a negative pole. The electromagnetic field produced by the microwaves oscillates as it passes through the water molecules, changing the polarity of the field and causing the dipole/water molecules to flip themselves in order to be aligned with the direction-reversing polarity millions of times a second. At the microwave frequency used in commercial systems (2,450 MHz), the dipoles align themselves and randomise at a speed of 4.9×10^9 times per second [12]. This molecular agitation and the friction of the water molecules reversing direction generate heat within the water medium. In the case of solution with ionic solutes, the ions create heat by colliding in the rapidly oscillating electromagnetic field, leaving less microwave energy available for dipole/water molecule to generate heat.

Water molecules are the most polar ones and absorb most of the emitted microwaves. Therefore, water appears to be the best solvent for MAE. The extraction occurs when the water absorbs energy coming from the microwaves and increases the pressure inside the plant material causing the cell structure to break allowing water to penetrate into the matrix and subsequently increases the extraction yield. This additional physical force to heat produced in the extraction medium contributes to increase the extraction yield [13].

Working on MAE Lucchesi et al. [14] observed by scanning electronic microscopy that the husk of cardamom seeds was clearly damaged after 1 h extraction time. At the end of the extraction, the authors noticed a great number of perforations on the external surface of the seeds and that some starch was also dispersed in the water-extraction medium. In the same way, Zhang et al. [15] showed that MAE created interstices on leaves of *Epimedium koreanum* and numbers of chloroplasts have been released from the plant cells, leading the water extract to turn from colourless to green.

MAE is now widely applied to extract from plant material many chemical compounds such as phenolic compounds [16–19], polysaccharides [20], terpenoids or essential oils [21, 22], alkaloids [15], saponins [23] and pectins [24]. MAE was also proposed as a new alternative to the conventional hydrodistillation technique for essential oil extraction, as this technology preserves heat-sensitive compounds because water heating is quicker than hydrodistillation. Extraction yields are generally found to be similar with those obtained with both techniques, but MAE may be completed in shorter operation times, several folds lower than those required

for hydrodistillation, for example. Essential oil composition obtained using these two techniques may be slightly different because of water solubility of some essential oil components that play a significant role in hydrodistillation but have no real effect when using the solvent-free MAE directly with fresh plant material.

Therefore, MAE has attracted significant attention in research and development of innovative applications for the extraction of natural products due to its special heating mechanism, moderate capital cost, high-throughput capability and good performance under atmospheric conditions.

13.2.1 Parameters of MAE

Besides the conventional parameters that characterise the operational conditions of a MAE trial (volume of extraction medium, solid–liquid ratio, trial duration, extraction temperature, etc.), microwave power is a specific one which has to be taken under consideration [15].

Usually, microwave power is a parameter, manually controlled, that affects directly the temperature of the extraction medium during MAE. Increasing the microwave power leads generally to increase the extraction liquid medium temperature, which in turn modifies the liquid physical properties, such as viscosity and surface tension. Compound extraction yield is modified and if heat-sensible compounds are present in the sample, they may also be affected by an extraction temperature increase. Power level has to be adjusted to the mass amount of sample to be extracted at the same time because the total microwave energy provided is shared among the different pieces of samples put at the same time in the extraction reactor, and each piece has to receive enough microwave energy so that extraction can occur. Power level applied has to be adapted to the sample weight involved and to the sensitivity of the compounds to be extracted [25].

Extraction time setting depends on the level of the microwave power applied. Combination of the two settings has in turn an effect on the temperature reached during the extraction trial and on the total energy delivered per sample weight unit. This combination has to be fine-tuned to speed up sample extraction by increasing as far as possible cell wall rupture and avoiding degradation of heat-sensitive extracted compounds. Therefore, MAE apparatus shows generally two manual settings:

- One setting to adjust the microwave power according to the total volume of extraction liquid and to the total weight of the sample to be extracted (weight/volume ratio or number of sample pieces)
- One setting to fix the extraction time to take into account the acceptable temperature rise during extraction [13]

Compared to conventional extraction techniques, MAE generally requires shorter extraction time to reach the same extraction results. When using a traditional MAE apparatus operating at 2,450 MHz frequency [12], it is widely recognised that a 10 min time is enough to complete the extraction [18, 26].

Fig. 13.7 Domestic microwave oven used for MAE laboratory-scale studies

13.2.2 Laboratory- and Pilot Plant-Scale MAE Apparatus

Most of the researches on MAE undertaken at laboratory level used a simple domestic microwave oven (Fig. 13.7). The apparatus is composed of a 20–25 L volume cavity/oven and uses a probe system delivering a microwave frequency of 2,450 MHz, and the variable power is generally limited within the range 500–1,000 W only. Power and time settings are provided to set the desired values before operation, according to the nature of the sample to be extracted.

Today, professional equipments are available from manufacturers and can be used for laboratory-scale researches. These apparatus provide regulation functions and various types of captors to control accurately and safely parameters and operation conditions during the extraction process. Milestone Inc. in Italy (www.milestonesci.com), CEM Co. (www.cem.com) in the USA and Sineo Microwave Chemistry Technology Co. in China (www.sineomicrowave.com) are examples of private sector developer manufacturers. These instruments can be classified into two types of systems: closed vessel and open vessel.

- The closed-vessel systems used for MAE consist of a magnetron tube placed on a turntable in an oven and equipped with only the necessary parameter controls. Generally, one manual setting is provided to adjust the maximum power to be delivered during the extraction trial and one setting to adjust the extraction duration, also displaying the running extraction time, and to end the process in case the maximum acceptable temperature in the extraction medium is reached, and a pressure control is coupled with the on/off control of the magnetron tube (Fig. 13.8). MAE closed-vessel systems, allowing sample extraction in pressurised vessels, were developed and marketed by Milestone Inc. These apparatus allow operating securely at higher temperature. They are equipped with a specific extraction vessel with a vent-and-reseal technology security (US Patent 5,270,010) that operates according to the three steps as shown (Fig. 13.9). The vessel cap is held in place by a dome-shaped spring (sketch 1). When an uncontrolled overpressure appends inside the vessel, the spring placed over the

Fig. 13.8 Closed-vessel microwave chemistry workstation (MDS-8G model, Sineo Co., China)

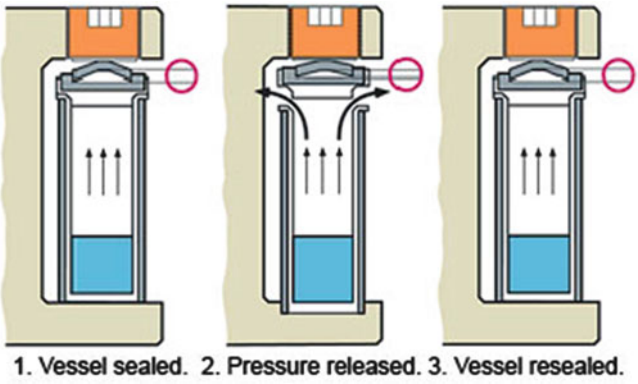

Fig. 13.9 Vent-and-reseal technology to secure the MAE vessel (According to [27])

vessel cap is flattened by the overpressure and the cap lifts up slightly, releasing the overpressure (sketch 2). Immediately after the overpressure released, the spring pushes down the cap that reseals the vessel (sketch 3), while the extraction process carries on and the vent-and-reseal system is ready to operate when needed. This technical improvement eliminates potent risks of vessel failure or explosion in case of a possible happening of an out-of-control exothermic reaction during MAE.

- MAE open-vessel systems are solvent-free technology. Such apparatus are mainly proposed by Milestone Inc. (NEOS and NEOS-GR models) (Fig. 13.10). The two models are equipped with a chamber with door, built in a material that does not allow microwave leakage to outside. This chamber is equipped with a magnetron probe and its built-in electronic control device. MAE takes place in this chamber. The vessel containing the sample to be extracted is placed in this MAE chamber. The NEOS model is equipped with a glass distillation system,

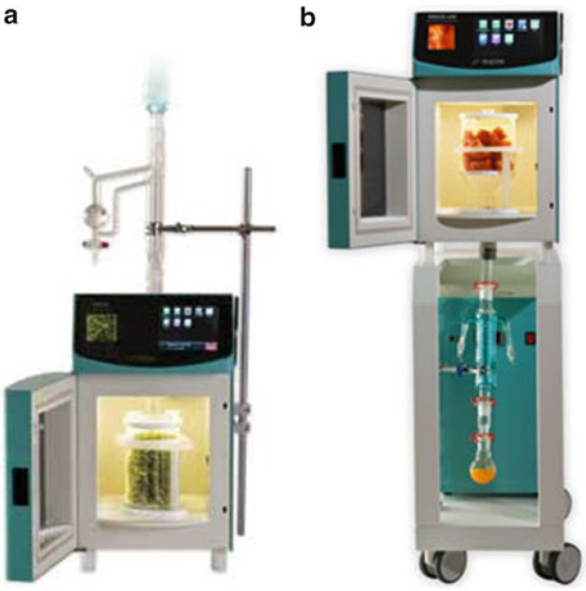

Fig. 13.10 NEOS (**a**) and NEOS-GR (**b**) models for MAE (Milestone Inc.)

watertight connected to the vessel placed in the MAE chamber (sketch a). In the NEOS-GR model, the MAE chamber is placed above another chamber. The facing bases of the two chambers are pierced to allow a communication glass tube to be placed. An extraction vessel placed into the upper MAE chamber is watertight connected through the glass tube to the glass system placed into the lower chamber. This system consists of glassware to collect the liquid extracted from the raw material in the upper MAE chamber. The NEOS-GR system is somewhat the upside down design of the NEOS system. In both systems, glassware is put in direct connection with the open air, avoiding any possible overpressure to occur during MAE.

The NEOS system was scaled up at pilot plant level by Milestone Inc. A semi-industrial-scale apparatus, MAC-75 model as shown in Fig. 13.11, was manufactured and is now marketed. The MAC-75 apparatus is a multimode microwave reactor. It is equipped with 4 magnetrons ($4 \times 1{,}500$ W total power, 2,450 MHz frequency) that can be set to various power levels set by 500 W increment levels. The stainless steel extraction chamber has a capacity of 150 L and contains a removable, rotating PTFE drum that allows up to 75 L of sample to be loaded in.

The industrial microwave apparatus are designed more often for dying and sterilisation. At a larger scale, industrial MAE line is mainly composed of microwave generators (Fig. 13.12a), such as those provided by Synotherm Co. (www.synotherm.net). These generators are attached with a specific design to open- or closed-type microwave chambers. A model of such an apparatus is developed by Yueneng Microwave Co. (www.pin-ba.com), as shown by Fig. 13.12b.

Fig. 13.11 Semi-industrial-scale MAE apparatus MAC-75 model (Milestone Inc., reprint from [28] with permission from Elsevier)

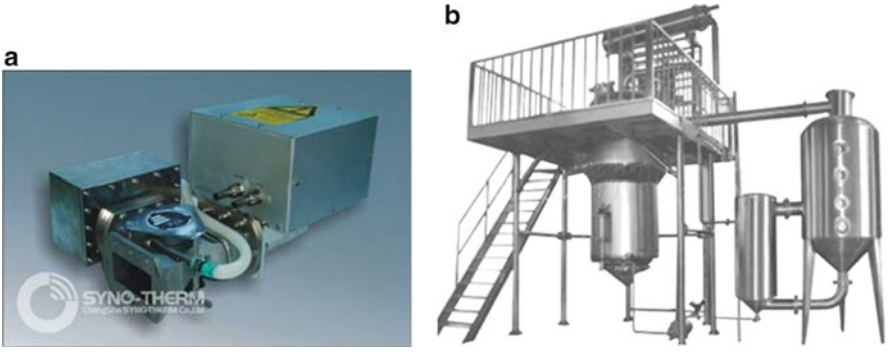

Fig. 13.12 Industrial-scale microwave generator (**a**) and MAE apparatus (**b**)

13.3 Pulsed Electric Fields Extraction (PEFE)

Pulsed electric fields (PEF) are a non-thermal emerging technology based on the application of external electric fields that induce damage to cell membranes (electroporation) with preservation of the intrinsic quality of the product processed, including purity, colour, texture, aroma, flavour and other nutritional components.

This technology has made its way from the laboratory to market. It opens new perspectives for the food industry. It can be used to preserve liquid bulk products such as fruit juice, milk, yoghurt and soup, by inactivating the microbial organisms they may contain [29]. The electric impulses can be applied homogeneously through

the product, and the technology is readily applicable for the pasteurisation of liquid foods at low temperature. Moreover, PEFE can speed up extraction of natural compounds, compared to traditional solid/liquid extraction [30]. Many researches have already demonstrated the progress brought to the efficiency of plant extraction using PEF technology [31–33]. Yin Yongguang et al. [34] reported that polysaccharide extraction using PEFE method gave higher yields compared to the others conventional extraction methods, such as alkali-based or enzyme-assisted extraction techniques. Eduardo Puértolas et al. [35] showed that grape treated by PEF before alcoholic fermentation gave a wine with higher colour intensity, better total polyphenol index (TPI) and higher total anthocyanin content (TAC) than wine obtained without PEF pretreatment. Moreover, coupling PEF with the fermentation process shortened about 48 h the grape maceration step, compared to the control classical process.

PEFE proceeds through mass transfer between the raw material to be extracted and the solvent. As the material to be extracted is generally from plant or animal origin, the valuable compounds to be extracted are generally enclosed in the cell tissues. The cell membrane is as a semipermeable barrier, playing an important role in compound exchanges towards the membrane. The membrane structure affects the selectivity and the speed of these exchanges. PEF treatment of such raw material reduces selectivity and increases permeability of the cell membranes of the material. PEF can also partially or totally destroy the cell membrane integrity, leading to higher and quicker mass transfer between the cell content and the surrounding solvent. This phenomenon, actively developed for applications in molecular biology and in medicine, is called electropermeabilisation or more commonly electroporation.

When a biological cell is exposed to external electric field strength, a time- and position-dependent transmembrane potential is induced across the non-conductive cytoplasmic membrane. This is the result of the accumulation of oppositely charged ions on both sides of the membrane. Under the effect of the electric fields, attraction between these ions occurs and causes reduction of the membrane thickness and even the formation of pores. A critical value of the external electric field is required to induce a transmembrane potential (0.2–1.0 V) that leads to the formation of reversible pores in the membrane. When a more intense PEF is applied, irreversible electroporation takes place, resulting in cell membrane disintegration as well as loss of cell viability [30].

In the food industry, products are generally preserved by heat treatments that killed the bacterial flora they may contain. PFE can produce irreversible electroporation if the level of PEF is high enough. Therefore, PEF can be advantageously used to kill all kinds of these undesirable endogenous biological cells. This is the reason why PEF has been extensively studied for non-thermal food processing providing microbiologically safe and minimally processed foods. As transmembrane potential is proportional to the radius of cell, the larger the cell, the greater the transmembrane potential. Thus, the electric field strength level required for electroplasmolysis has to be adapted to the cell size. It was also successfully applied to disintegrate biological

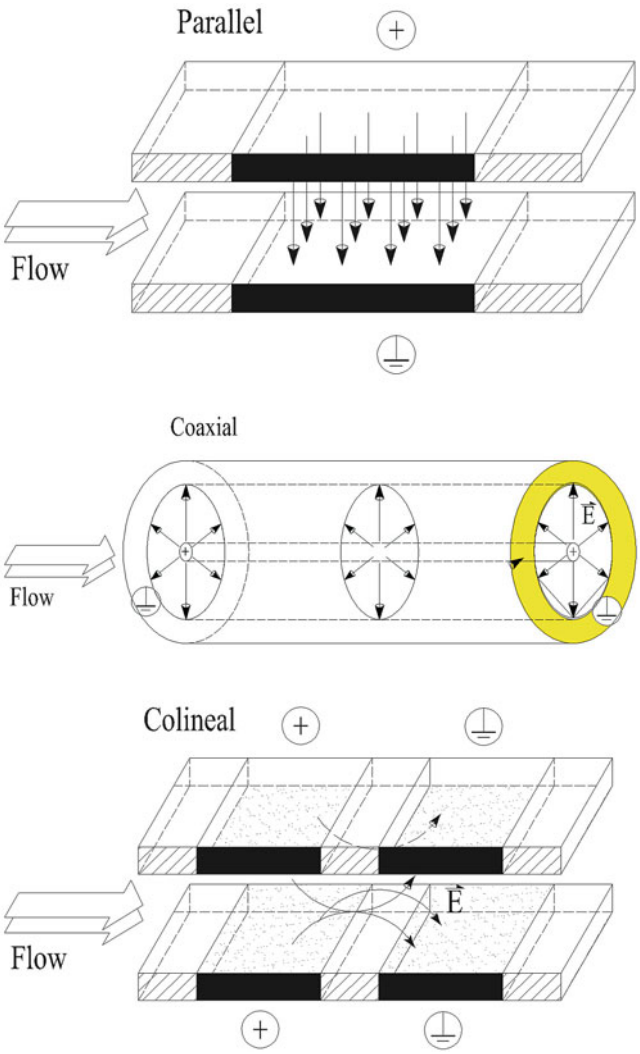

Fig. 13.13 Designs of treatment chambers built-in commercial PEFE apparatus

tissue to improve the release of intracellular compounds during extraction of vegetal sample. Generally, for plant cell, the electric field strength required is about 0.5–5 kV/cm [36].

The two components of a PEF-based apparatus are the pulse generator and the treatment chamber. Different treatment chamber designs have been developed in the past few years. Today, the three most important chamber designs kept in the development of commercial PEF apparatus are configurations showing parallel electrodes, coaxial electrodes and colinear electrodes (Fig. 13.13) [36].

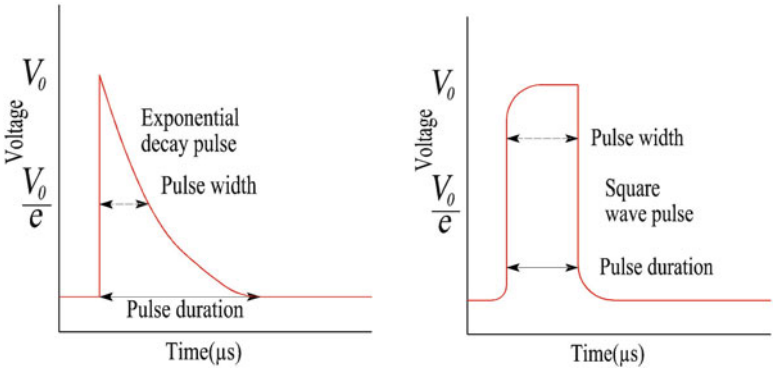

Fig. 13.14 Most usual pulse shape uses in common PEFE applications

13.3.1 Parameters of PEFE

The most typical process parameters that characterise PEF technology are electric field strength, pulse shape, pulse width, number of pulses, frequency and pulse-specific energy. The distance between the electrodes of the treatment chamber and the voltage delivered define the strength of the electric field (E, in kV/cm units). The most usually used pulse shapes are those with exponential decay or with square waveform, as shown in Fig. 13.14. Square waveform geometry has been determined to be the ideal pulse shape for PEF processing because in this configuration, the electric field intensity remains constant within the pulse duration. The treatment time for a PEF application is defined as a product of the pulse width and number of pulses applied. The frequency (f) is the number of pulse per second (Hz).

The specific energy (W) of the pulse depends on the voltage applied, on the treatment duration and on the ohmic resistance of the volume of the product filling the treatment chamber, limited by the electrode length. This resistance is a function of the geometry and the conductivity of this product volume. The specific energy is calculated according to Eq. (13.2), and its value allows to evaluate the energy cost of the PEFE process:

$$\begin{aligned} &W = \frac{1}{m}\int_0^{\infty} k \cdot E(t)^2 \mathrm{d}t \\ &m = \text{material mass (kg)}; \quad t = \text{treatment time (s)} \\ &E = \text{strength of the electric field } \left(\mathrm{kV \cdot cm^{-1}}\right) \\ &k = \text{eletrical conductivity of the material treated } \left(\mathrm{ms \cdot cm^{-1}}\right) \end{aligned} \tag{13.2}$$

PEFE using water as solvent was studied to extract various bio-compounds from different natural substrates, such as colourant compounds [33, 37, 38], sucrose [32], polysaccharides [34], phenols [3, 39], podophyllotoxin [40], water-soluble compounds from microalgal biomasses [41], fennel [42] and chicory [31].

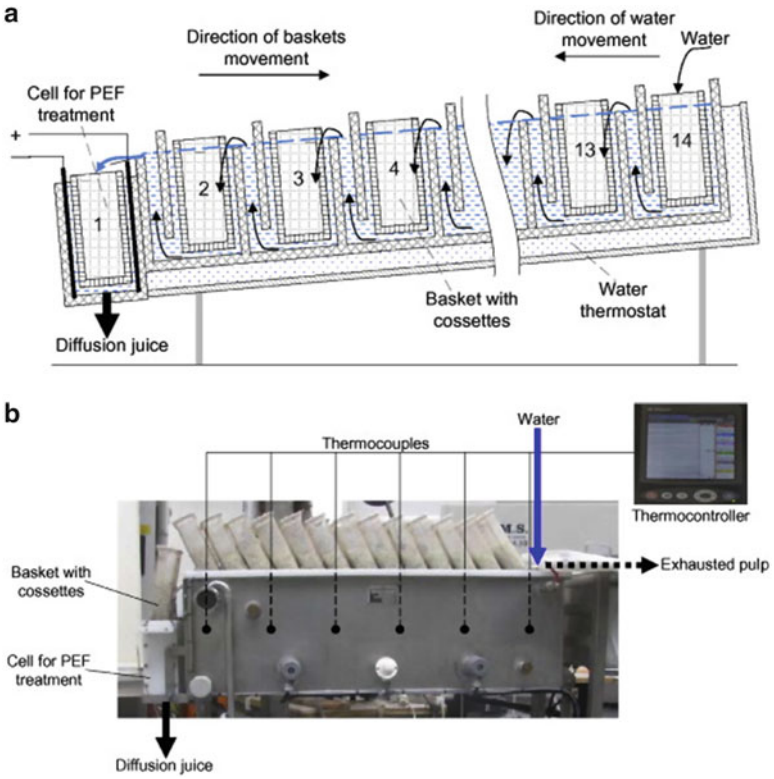

Fig. 13.15 Countercurrent PFE water extractor: (**a**) schematic representation and functioning principle, (**b**) picture of a pilot-scale apparatus (Reprint from [43] with permission from Elsevier)

13.3.2 Applications of PEFWE at Pilot Plant Scale

Pulsed electric field-assisted water extraction (PEFWE) is not yet applied at the industrial scale because there is a lack in the technology dealing with high-voltage pulse generation at an industrial scale. Nevertheless, some PEFWE units were yet developed at pilot plant scale.

The team of Eugène Vorobiev [43] developed an application of PEFWE to extract sugar from sugar beets. A pilot plant scale countercurrent cold and mild heat extractor was built. It consists 14 extraction sections set in series, as shown in Fig. 13.15. The PEF treatment chamber (section 1 of the extractor) was specially designed and isolated from the other sections. Section 1 was equipped with two stainless steel electrodes to generate PEF. The sugar beet roots were cut into cossettes and filled in the baskets and then placed in the 14 extraction sections. The 14 sections of the apparatus were filled with running water from the last and upper section (i.e. section 14) down to the lower PEF section (i.e. section 1). The first basket with sugar beet cossettes was submitted to PEF treatment in section 1 for

5 min, and then baskets were moved manually between the neighbouring sections. The process continue in such a way that the baskets with sugar beet cossettes moved from one section to the other and water was added to the last section 14 to contact with most exhausted cossettes every 5 min also in the opposite direction (countercurrent flow). Each basket was filled with 0.5 kg of cossettes, and in each section, the solid/liquid ratio was set as 1:1.2. The output water flow running out from the PEF section 1 was enriched in extracted sugar by water diffusion during its percolation through the 14 sections of the apparatus. This diffusion juice was collected for further treatments.

The total time of diffusion can be calculated as $t_d = 14 \times 5 \text{ min} = 70 \text{ min}$. Water temperature was varied from 30 to 70 °C, which was controlled by the thermocontroller inside the extractor. The temperature of cossettes at the input of extractor was $T = 10$–13 °C.

This apparatus equipped a pilot plant-scale PEF generator (Hazemeyer, 5,000 V, 1,000 A, France). It provided monopolar pulses with a near-rectangular shape signal and the electric field intensity used was $E = 600 \text{ V} \cdot \text{cm}^{-1}$ when operating at 30 °C and was $E = 260 \text{ V} \cdot \text{cm}^{-1}$ at 60 °C. A train of pulses consisted of 500 successive pulses of 100 μs duration each and repetition pulse of 5 ms intervals. Only one train of pulses was used for a 50 ms PEF treatment of every set of sugar beet basket, which corresponds to 5.4 $\text{kW} \cdot \text{h} \cdot \text{t}^{-1}$ energy input. Temperature elevation during each PEF treatment cycle did not exceed 3 °C, making this PEFWE to be considered as a low or moderate thermal extraction process. The juice purity (sucrose/total soluble solid content) was not lower than those obtained by conventional hot water diffusion (70 °C) of sugar beet cossettes.

The team of Javier Raso studied the influence of PEF treatment on wine making at laboratory and pilot plant levels [35, 44–47]. They showed that phenol extraction from grapes, specifically anthocyanin compounds, can be improved by using PEF pretreatment. They confirmed that the same results were obtained when scaling up the process at pilot plant level; they thought that the process could be used at an industrial-scale level as an innovative use of PFE-assisted extraction for wine making. Therefore, a PEFE equipment was built (Modulator PG, ScandiNova, Uppsala, Sweden) which generates square waveform pulses of a width of 3 μs and a frequency up to 300 Hz [46]. The maximum output voltage was 30 kV and current intensity was 200 A. Cabernet Sauvignon grapes were processed using a continuous flow PEF treatment.

The extractor was equipped with a colinear type treatment chamber showing two successive treatment zones of 2 cm long and 2 cm inner diameter each, positioned between ground and high-voltage electrodes, as shown in Fig. 13.16a. The applied electric field strength is not uniform along the 2 treatment zones but shown symmetrically placed force lines, as shown in Fig. 13.16b. The grape pomace was pumped in the colinear treatment chambers at a mass flow rate of 118 $\text{kg} \cdot \text{h}^{-1}$, using a progressive cavity pump (Rotor-MT, Bominox, Gerona, Spain). PEF treatment consisted in an average of 50 pulses of an electric field strength of 5 $\text{kV} \cdot \text{cm}^{-1}$ (total specific energy: 3.67 $\text{kJ} \cdot \text{kg}^{-1}$) at a frequency of 122 Hz.

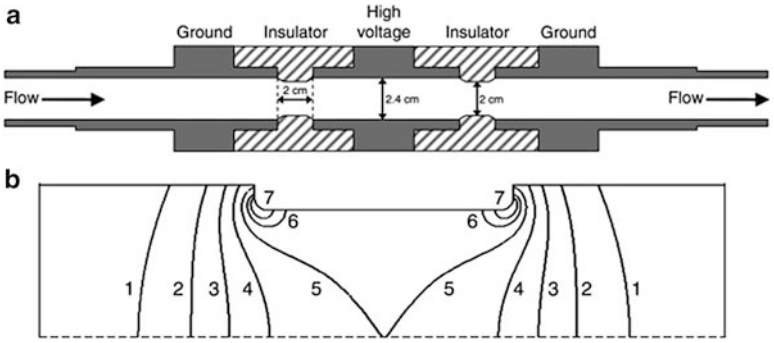

Fig. 13.16 (**a**) Scheme of the colinear PEF treatment chambers, (**b**) finite elements method simulation of the electric field line distribution from the weakest (1 $kV \cdot cm^{-1}$) to the strongest electric field strength (7 $kV \cdot cm^{-1}$), input voltage = 14.2 kV of the upper half part treatment zone of one chamber (Reprint from [46] with permission from Elsevier)

In this work, it was shown that an increase of the electric field from 2 to 7 $kV \cdot cm^{-1}$ leads to an extraction rate increase of both anthocyanins and total phenols.

13.4 Negative Pressure Cavitation Extraction (NPCE)

The negative pressure cavitation (NPC) technology was invented by the team of Yu-jie Fu, at Northeast Forestry University, Haibin, China [48].

Cavitation is produced by pressure forces acting upon the liquid leading to the formation of vapour cavities (small liquid-free volumes or bubbles) within this liquid medium. This phenomenon occurs when a liquid is subjected to rapid changes of pressure leading to the formation of cavities where the pressure inside is low. When subjected to higher pressure, the cavities collapse rapidly and generate an intense shockwave. Cavitation serves as a means to concentrate in very short time in a region that diffused fluid energy to create a zone of intense energy dissipation. Ultrasounds applied to a liquid medium can generate such a phenomenon. Cavitation effects can also be produced by acoustic and hydrodynamic means.

NPC is another type of technique to generate cavitation. It uses negative pressures, and its intensity is not weaker than that produced by ultrasounds. Zhang et al. [49, 50] compared the morphological change of pigeon pea roots treated by these different techniques. They showed that the root cell walls were more destroyed using NPC cavitation than using ultrasounds. Liu et al. [51] compared the extraction efficiency obtained using four techniques: NPC, ultrasounds, microwaves and reflux. They concluded that NPCE showed an equivalent extraction efficiency as UAE which was more effective than MAE and reflux extraction. Moreover, the UAE

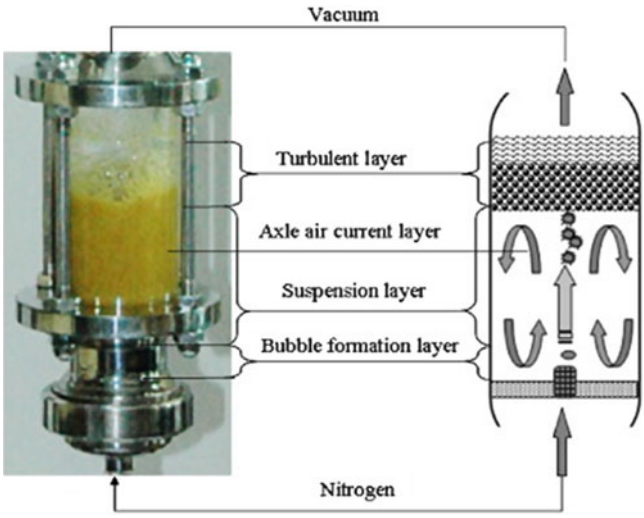

Fig. 13.17 Layer distribution within an extraction medium submitted to NPC (Reprint from [52] with permission from Elsevier)

produced a great amount of heat, as NPCE kept the extraction medium temperature at its initial level, which was in favour of the extraction of heat-sensitive products [50]. NPCE appeared also to be a cheap and energy efficient process to extract natural products.

13.4.1 Mechanism and Parameters of NPCE

The mechanism that occurs during NPCE consists of successive formation and collapse of tiny bubbles under the action of vacuum within the liquid extraction medium placed in an extraction vessel along with the solid sample to be extracted (pieces or powder of raw material). Four layers can be distinguished from bottom to top of the extraction vessel: bubble formation layer, suspension layer, axle air current layer and turbulent layer. When nitrogen gas is continuously introduced into the extraction vessel, small nitrogen bubbles appear under the action of negative pressure caused by light vacuum applied into the vessel (Fig. 13.17) and ascend through the liquid–solid medium. This results in the formation of a highly instable gas–liquid–solid system. The suspension layer is formed and is located a little higher than the bubble formation layer. The tiny bubbles enter this suspension layer and grow rapidly because of the negative pressure created locally in this area, until they suddenly collapse, producing a cavitation phenomenon with intense collisions

so that the surface of the surrounding raw material particles is corroded. The extraction liquid can diffuse more easily into the solid particles, enhancing diffusion of extractible compounds. Higher in the vessel, intense vertical motion created in the axle air current layer helps extracting compounds from the sample material which is completed in the turbulent upper layer situated near the source of vacuum. Thereby, NPCE creates intensive cavitation-collision, turbulence, suspension and interface effects that combine to form a dynamic mass transfer enhancing extraction and accelerate mass transfer of targeted compounds from the sample solid matrix to the solvent [49, 50, 52].

The parameters that affect the efficiency of NPCE are the negative pressure, the nitrogen-gas flow, the particle size of the solid sample to be extracted, the extraction time and the liquid–solid ratio.

According to the NPCE mechanism, successive formations and bursts of bubbles in the liquid medium depend on the vacuum level created (negative pressure). The cavitation phenomenon generally occurred when the vacuum is set between −0.01 and −0.09 MPa. Zhang et al. [52] reported that a decrease of the negative pressure from −0.02 to −0.05 MPa enhanced the extraction yield of flavonoids from *Dalbergia odorifera*, and once the pressure was set lower than −0.05 Mpa, the extraction yield decreased slightly.

Nitrogen-gas flow is another key parameter in cavitation technique that affects extraction efficiency. Liu et al. [51] investigated the effect on the extraction yield of five flavonoids extracted from pigeon pea leaves submitted to NPCE. They observed a yield increase when the nitrogen-gas flow was set within the range of 10–40 $mL \cdot min^{-1}$, with an optimised gas flow 30 $mL \cdot min^{-1}$, to get the highest extraction yield.

13.4.2 Laboratory- and Pilot Plant-Scale NPCE Apparatus

The NPCE laboratory-scale device was designed and patented (Patent CN2597047) by the team of Fu [51]. It consisted of an extraction pot (1), a collection pot (2), a vacuum pump (4) and a nitrogen stock vessel (9). The extraction pot and the condenser (5) were glass made, as the other parts were steel made. The 400 mL volume extraction pot was a 17 cm high and 5.5 cm inner diameter cylinder (Fig. 13.18). Solid samples and solvent were added into the extraction pot through the inlet (3). The negative pressure was generated by a vacuum pump, and the nitrogen gas was introduced through the bottom valve (4). After NPCE, the solvent was collected in the collection pot (2) and filtered, and the residue was discarded.

A NPCE pilot plant-scale apparatus was developed by the same team [48]. The apparatus showed the same types of elements as those described for the laboratory-scale device, and a heating system was added to allow working at high temperature (Fig. 13.19). The working extraction volume was brought to 10 L.

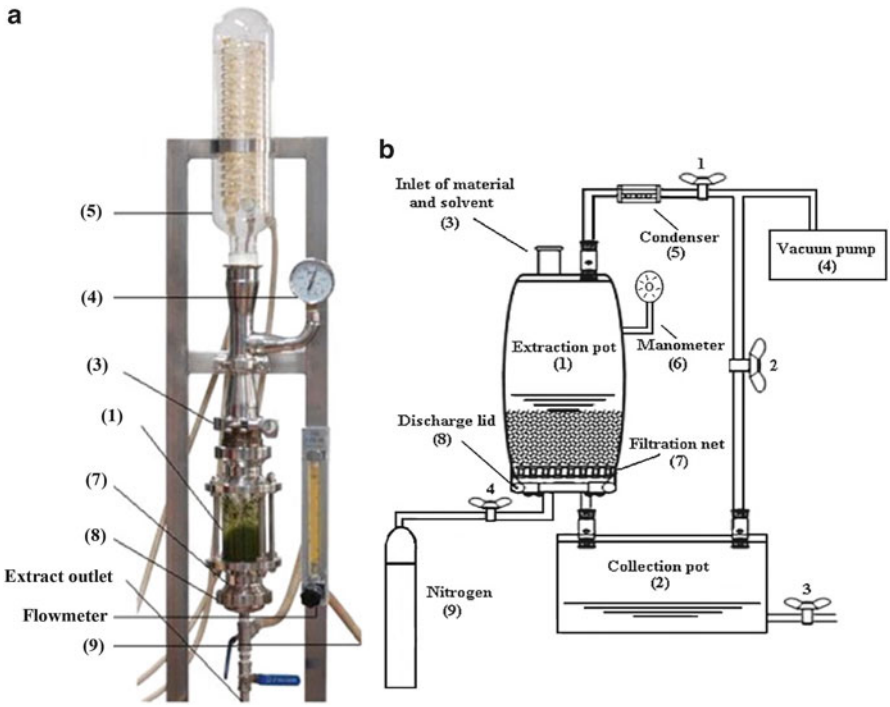

Fig. 13.18 NPCE apparatus: schematic representation (**a**) and laboratory-scale unit (**b**) (Reprint from [50] with permission from Elsevier)

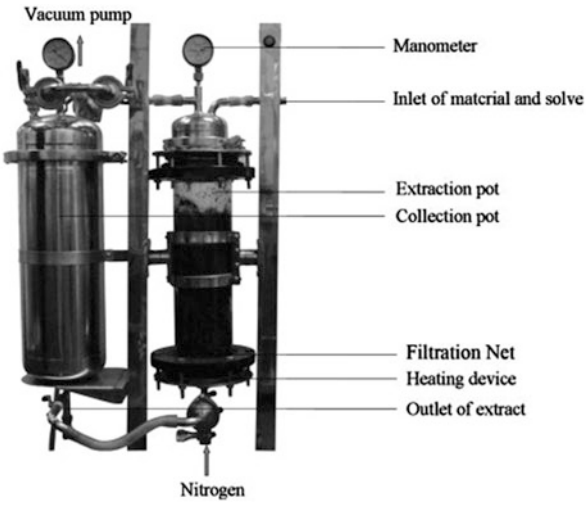

Fig. 13.19 Pilot plant-scale NPC extraction device (Reprint from [48] with permission from Elsevier)

13.4.3 Application of NPCE at Pilot Plant Scale

Since the NPCE technology has appeared for only 4 years, NPC applications were not largely developed and NPCE is not widely used today. Only laboratory-scale extractions of flavonoids and of other phenol compounds with antioxidant capacities were studied and recently reported in the literature [49–52].

The only application of NPCE conducted at pilot plant level was the extraction of the three main flavonoids (genistin, genistein and apigenin) from the pigeon pea roots [48], using the device descried in the previous chapter (13.4.2). The extraction conditions were firstly optimised at the laboratory scale using an optimisation experimental design (Box–Behnken design). An ionic solution was used as the extraction medium. Combinations of five kinds of anions (Cl^-, Br^-, $H_2PO_3^-$, HSO_4^- and BF_4^-) associated with 1-R-3-methylimidazolium cations (radicals R being alkyl groups which chain length increased from ethyl to octyl) were compared [48]. [C_8mim]Br ionic aqueous solution with a concentration of 0.53 $mol \cdot L^{-1}$ was chosen as solvent. The optimised conditions for NPCE were: temperature = 74 °C, negative pressure = −0.07 MPa, liquid–solid ratio = 20:1 $mL \cdot g^{-1}$ and the extraction time was 15 min. Five hundred grams of pigeon pea roots were extracted in the pilot plant NPCE apparatus. Extraction yields for genistin, genistein and apigenin were, respectively, 0.477 ± 0.013, 0.480 ± 0.014 and 0.271 ± 0.021 $mg \cdot g^{-1}$. As these yields were similar to those obtained using the smaller laboratory-scale device, the authors concluded that the NPCE method could be scaled up for applications at industrial-scale level.

13.5 Pressurised Hot Water (PHW) Extraction (PHWE)

Pressurised liquid extraction, using heated water as the extraction medium (solvent), is frequently named pressurised hot water extraction (PHWE). It is considered as another emerging green extraction technology for different classes of compounds present in numerous kinds of matrices such as environmental, food and botanical samples. This technique is also known under different names, such as pressurised solvent extraction (PSE), accelerated solvent extraction (ASE) or enhanced solvent extraction (ESE).

Water is a highly polar solvent (high relative permittivity $\varepsilon_r = 80$), and when it is heated at high temperature with enough pressure to maintain water in liquid form, which is named pressurised hot water (PHW), its physical properties are changed. Its relative permittivity falls ($\varepsilon_r = 35$ at 200 °C), near those of simple alcoholic solvents, such as ethanol ($\varepsilon_r = 24$) or methanol ($\varepsilon_r = 33$ at 25 °C), making water as good solvent as some organic ones. Thus, water becomes to be able to dissolve a wider range of compounds including low-polarity organic ones. PHWE stands as a good alternative to reduce utilisation of some organic solvents for liquid extractions that traditionally used them.

The term ‘pressurised hot water’ (PHW) is used to denote the region of condensed phase of water between the temperature ranges from 100 °C (boiling point of water) to 374 °C (critical point of water). It has been reported as subcritical water, superheated water, near-critical water and pressurised low polarity water.

In the PHWE technique, the raw material sample, placed in a metallic pressure-resistant cylindrical cell, is put into contact with the PHW, playing the role of a chromatography eluant. As pressure has to be increased to maintain water in its liquid state at the high working temperature, the targeted compounds present in the sample may partition themselves between the sample matrix and the percolating liquid (PHW). They are chromatographically eluted out from the cell into the pressurised collection vial.

Lots of published papers showed that PHWE appeared as powerful technique for water extraction of essential oils [53], proteins [54], polysaccharides [55, 56], anthraquinones [57], lignans [58], terpenes [59], low-polarity flavonoids [60], phenolics [61], microbial lipids [62] and organic pollutants such as PAHs, PCBs, pesticides, herbicides, etc. [63]. Efficiency of PHWE was also compared with other extraction technologies, such as microsound-assisted extraction, sonication-assisted extraction, Soxhlet extraction or other traditional reflux mode extractions. It was reported that PHWE was as powerful as these traditional technologies and, in some cases, was even more efficient [64].

13.5.1 Parameters of PHWE

The parameters that affect extraction efficiency of PHW technique include temperature of the liquid-state pressurised water, extraction time, water flow rate and use of extraction technical helps such as a small percentage of organic solvents or surfactants [65].

Water temperature used for extraction is the most important parameter which could affect extraction efficiency and selectivity of PHWE. When increasing water temperature, water physicochemical properties change significantly: decrease of its relative permittivity and reduction of its viscosity and surface tension. Hence, raising the working temperature modified the polarity of the extracting water, which turns it into a specific solvent for low-polarity compounds. As water viscosity is reduced and water surface tension increased, diffusivity of the extracting water is significatively enhanced, allowing water to enter more easily the sample matrix, leading to a better mass transfer between water and the sample. But decomposition of heat-labile extracted solutes can occur due to the applied high temperature and pressure.

Working temperature was found to be a selectivity factor in PHWE as shown by M. J. Ko et al. [60] in studying its application for flavonoids extraction. The optimal extraction temperature for flavonoid aglycone with an OH side chain, such as quercetin, was found to be 170 °C. For aglycone compounds with an O-CH_3, as

in isorhamnetin, or with a H group, as in kaempferol, or for apigenin, with double bonds, the optimised extraction temperature was found to be 190 °C. Flavonoid glycoside forms were better extracted at lower temperatures: 110 °C for quercitrin, a glycoside form of quercetin and 150 °C for spiraeoside and isoquercitrin.

Alicia Gil-Ramírez et al. [66] compared the extraction yields of isoxanthohumol at different extraction temperature (50, 100, 150 and 200 °C). They found that the highest yield was obtained at 150 °C.

Benito-Román et al. [55] showed that 155 °C was the optimal temperature in PHWE of β-glucans of high molecular weight. Above 160 °C, the yield of β-glucans dissolved in extracting water decreased. Cacace et al. [58] found that maximum amounts of lignans and other flaxseed bioactive compounds, including proteins, were best extracted at 160 °C and phenolic compounds at 140 °C.

Yu Yang et al. [59] studied the stability of five terpenes during PHWE. They showed that terpene degradation became more serious when water temperature increased, and there was a significant drop of the extraction yield when water temperature was set around 200 °C, but yields were quite similar at both temperatures 100 and 150 °C. Chunhui Deng et al. [53] observed that the best extraction efficiencies for three active terpenoids compounds, camphor, borneol and borneol acetate, present in *F. amomi* samples were obtained at 160 °C.

Effect of pressure on PHWE yields is more limited than that of temperature [55]. In general, liquids are highly incompressible in their subcritical states. At constant temperature, pressure variation does not modify so much water solvation power, making pressure parameter to have a lesser effect than temperature in PHWE processes. Pressure is only used to maintain extraction water in its liquid state, according to the working temperature used. Moderate pressures such as 15 bar at 200 °C or 85 bar at 300 °C are enough to maintain water in its liquid state. Within this pressure range, Chunhui Deng et al. [53] did not found much change in extraction yields of the three terpenoids extracted from *Fructus amomi*, a traditional Chinese medicinal plant. In most published works on PWHE of natural products, the working pressure was kept within the range 10–50 bar [67–69].

PHWE can be performed in two modes: (1) the static mode where the sample is just put into contact with water under the working temperature and pressure chosen and (2) the dynamic mode where the water is percolated at a certain flow rate towards the sample.

In the static mode, extraction duration depends strongly on the extraction temperature and on the nature of the sample matrix and of the compounds to be extracted. Extraction time during PHWE of β-glucan from waxy barley flour was practically limited to 45 min when extraction temperature was set between 155 and 160 °C. The highest yield (53.7 %) was obtained after 18 min extraction time [55]. Rovio et al. [70] investigated at different temperatures the extraction kinetics of eugenol and eugenyl acetate from clove. They found that, at 125 °C, 80 min extraction time was needed to completely extract the two terpenes, but only 15 min was enough to obtain the same result when the working temperature was set at 250 °C or at 300 °C.

In the dynamic mode of PHWE conducted at a laboratory scale, water flow rates between 1 and 1.5 ml/min were used [67, 68]. But they may be out of this range in some experimental trials. In PHWE of lignans from flaxseed (*Linum usitatissimum* L.), using three extraction cells of 7.0, 9.4 and 19.3 mm i.d. and 10 cm long, the optimal water flow rate was found to as low as 0.5 mL/min [58]. On the opposite, the water flow rate has to be set at a higher value of 5 mL/min to obtain the best extraction yield for anthraquinone extraction [57].

In some cases, organic or inorganic additives have been used along with water in PHWE to improve compound recovery. Ju and Howard [61] have compared grape skin PHWE with and without adding sodium metabisulfite in the extraction water to obtain anthocyanins and other antioxidant-active compounds. They showed that 1,400 μg/mL sodium metabisulfite added to the extraction water improved extraction contents of total anthocyanins and total phenolic. Eng et al. [71] evaluated the assistance of surfactant for glycyrrhizin and ephedrine PHWE. They found that adding anionic surfactant such as SDS to the extraction water enhanced the solubility of the targeted compounds into the mobile phase and therefore higher extraction yields were obtained.

13.5.2 Laboratory- and Pilot Plant-Scale PHWE Apparatus

There is not yet marketed PHWE apparatus to our knowledge. At laboratory scale, this type of equipment is normally designed and built by researcher teams themselves from a specific technical adaptation of already existing commercial equipments, such as for accelerated solvent extraction (ASE) or supercritical fluid extraction (SFE) [67].

Briefly, two major types of PHWE apparatus are built on the operating principles related to the static and the dynamic extraction modes.

Apparatus working on the dynamic extraction mode are composed of the following parts: a pressurised solvent tank to supply water to the system, a pump for pushing the solvent through the extraction cell containing the sample to be extracted, a heater device to provide the system with the desired operation temperature, the extraction cell consisting of a high-pressure-resistant cylinder where the solvent and the sample are put together into contact for extraction to occur, a pressure control device coupled with a back-pressure regulator and a collection vessel to recover the extract (Fig. 13.20). The extraction vessel is usually a stainless steel cylinder having 10–15 cm long and an internal diameter of 7–20 mm and 10 mL total volume. The high-pressure pump pressurises the water (extraction solvent) and pushes it through the sample at a constant flow rate. Temperature of the extraction vessel is maintained at the chosen value by various means such as GC ovens, sand baths or resistive heating blocks [69, 72–74].

In the extraction vessel, the sample has to be finely dispersed by mixing it in a powder form with a certain quantity of sand or other inert material to prevent any possible clogging during solvent percolation through this bed of mixed particles. As

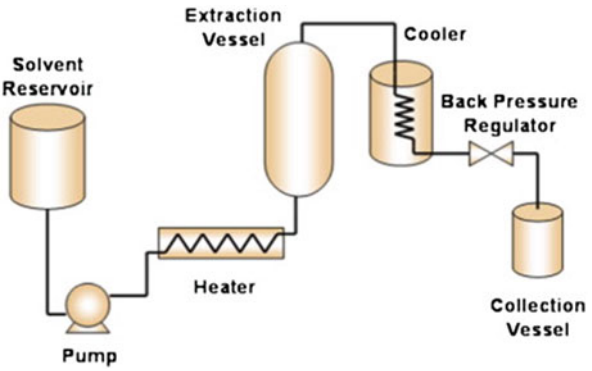

Fig. 13.20 Schematic diagram for PHWE (Reprint from [72] with permission from Elsevier)

plant particles have a general tendency to absorb some quantity of water leading to some bed compression, the inert material added facilitated water percolation monitored by the pumping system during the course of the extraction.

Apparatus working on the static extraction mode are now marketed by Thermo Scientific (www.thermoscientific.com). An illustration of such apparatus is the commercial laboratory-scale ASE® equipment proposed as one model of the Dionex ASE system (www.dionex.com) (Fig. 13.21). Several models are offered: ASE 100 and ASE 150 system equipped with a single extraction cell, ASE 300 system with 12 cells, ASE 200 and ASE 350 systems with 24 cells. The newest model, Dionex ASE 350 system, is an apparatus that automatically extracts up to 24 samples (of 1–100 g each) and accommodates various cell sizes of 1, 5, 10, 22, 34, 66 and 100 mL volume.

Pilot plant-scale equipments for PHWE were scaled up from the design of the laboratory-scale apparatus [72]. Lagadec et al. [75] scaled up a PHWE system to remove contamination products from soils using a super large extraction vessel of 102 mm i.d. × 1,000 mm long, which size is about 10 times bigger than those of the laboratory-scale extraction vessel. The capacity of such a vessel is about 1,000 times compared to those of a laboratory-scale unit. This allows extraction of more than 8 kg of soil sample per extraction cycle, compared to only 8 g sample that can be extracted in a laboratory-scale apparatus. Water was heated by a propane heater and the extraction cell is maintained in temperature using a thermocouple-controlled heating tapes rather than using an oven. The hot water flow rate was set at 0.5 L/min for the pilot-scale extractor.

13.5.3 Application of PHWE at Pilot Plant Scale

Irene Rodríguez-Meizoso et al. [76] applied PHWE at pilot plant scale to extract antioxidant compounds from rosemary leaves. They developed an original system for PHWE, including an on-line drying system: continuous PHWE of rosemary leaves followed by a continuous production of an aerosol created from the extract

Fig. 13.21 Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor

by a supercritical CO_2 nebulisation system. This aerosol was injected in the particle formation chamber along with a hot N_2 gas flow which instantaneously dried the aerosol, and particles of extract compounds were immediately formed in the chamber (Fig. 13.22).

Water was pumped as the extraction solvent, into the extraction vessel, using a modified Suprex Modifier pump. Extraction cell and inlet/outlet tubing connected to the vessel were placed inside a GC oven (Carlo Erba Strumentazione, Milano, Italy) to maintain the extraction temperature at the required level (200 °C) that allowed maximal extraction of antioxidant-active compounds. The extraction cell was filled with a mixture of solid particles of grinded rosemary leaves and washed sea sand. The process starts by filling the extraction cell with water at room temperature. Then, the CO_2 injection and the heating systems are started together. When the starting working conditions were reached (80 bar, 2–3 mL/min CO_2 and 200 °C cell-temperature), N_2 injection was started at a pressure of 6–7 bar and water is pumped at a constant flow rate (0.1–0.3 mL/min) through the particle bed placed in the extraction cell. With such an extraction system, 10 g rosemary extract was obtained from 29.4 g of rosemary leaves using only 382 mL water. The extract obtained was enriched in carnosic acid, an antioxidant-active compound of rosemary leaf [75].

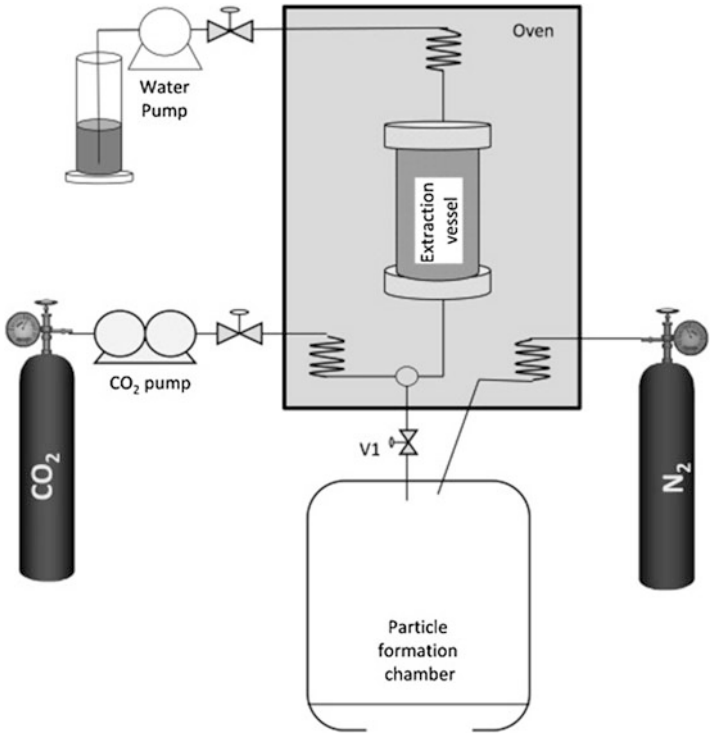

Fig. 13.22 Pilot plant-scale PHWE system developed by Irene Rodríguez-Meizoso et al. (Reprint from [75] with permission from Elsevier)

13.6 Membrane-Based Separation and Extraction

Classical water extraction (maceration, infusion, decoction, etc.) of solid sample material such as plant needs generally large volumes of water, and the bulk extract obtained is generally a mixture of water-soluble compounds, of macromolecules in colloidal state and of water-suspended insoluble particles. If the water-soluble compounds remained not only the interest extracted compounds, they have to be separated from other matters present in the extraction water. In further process steps, they can be purified and concentrated. Several separation techniques are available today to perform successfully all these additional technological steps that are often needed to complete a water-extraction process chain. Among them, membrane separation technology offers a certain number of advantages for the separation, the purification, and the concentration of very valuable and heat-sensitive water-extracted compounds. They can be applied in all these additional process steps. Membrane-based separation is an emerging technology adapted for the posttreatment of a global water extract since this technology can operate at room temperature and avoid any phase change of the extracted products. Moreover,

this technology is claimed to be more energy-saving than conventional thermal separation/concentration processes such as evaporation, distillation, sublimation or crystallisation. Major membrane separation techniques (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) have nowadays found lots of specific uses and applications in different industrial sectors. They are based on physical separation technique according to the filtration principle, leading, from a liquid medium or from a raw material extract process, to two output fractions, namely, permeate and retentate. Both of them can be used further to recover the valuable extracted products of interest they may contain.

13.6.1 General Considerations About Membrane Technology

With nearly 50 years of rapid technological development and progress, membrane-based processes enjoy today numerous of industrial applications that have brought great benefits to human life. These applications include water purification, dairy standardisation and stabilisation, sea and brackish water desalination, wastewater reclamation and reuse, food and beverage production, gas and vapour separation, energy conversion and storage, air pollution control and hazardous industrial waste treatment, hemodialysis, protein and microorganism separations, etc. The scope of membrane technology applications is still extending and is stimulated by numerous developments of novel or improved materials and separation membranes with better chemical, thermal and mechanical resistant properties and better permeability and selectivity characteristics, as well as by a significant decrease of capital and operation costs. Development of novel applications using membrane separation technology is however closely dependent of the future development of the heart of the membrane process: the membrane itself with new intrinsic and specific physical characteristics.

Generally speaking, a membrane is a barrier of a few hundred nanometres to several millimetres thick to separate two phases and to be able to allow a selective transfer of various components.

Separation membranes can be classified into two types, according to the internal structure of the material they are made of. The first type is the isotropic membrane group: they are microporous and non-porous membranes characterised by constant structural properties along the entire membrane thickness, i.e. pore sizes are small and relatively constant throughout the membrane thickness. In separation process, these membranes act as depth filters, the solution move by diffusion through the membrane and small particles in suspension in the solution may be retained in their internal structure, resulting in clogging the membrane and reducing filtration fluxes.

The second type is the anisotropic (asymmetric) membranes group: the membrane material shows a composite structure consisting of a number of layers, each with different structures, pore sizes, and permeabilities. The anisotropic membrane has a relatively dense, extremely thin and dense surface layer (i.e. the ‘skin’,

also called the permselective layer) with constant pore sizes, which characterise the average pore size and the selectivity of the overall filtration membrane. The permselective layer is supported on a much thicker porous substructure showing good flux, to withstand the compressive forces used in the separation or filtration process. The thin layer is always on the high-pressure side of the membrane (the feed side). These membranes had the advantage of higher transfer fluxes, and almost all industrial processes use such membranes.

The liquid membranes can be also placed in this group. They consist of a liquid phase (e.g. a thin oil film), either in supported or unsupported forms that serve as a membrane barrier between two phases of aqueous solutions or gas mixtures.

Membrane separations are physical separation, compared to other separation and concentration techniques. Membrane separations are attractive for industrial because (1) membrane processes are suitable for filtration of liquids containing sensitive products. The filter is a physical membrane that operates without addition of any chemicals and is an absolute barrier for many types of compounds. Concentration of biological, nutritional and organoleptic compounds at low temperature by membrane separation is more favourable than thermal evaporation operations; (2) the membrane unit is modular and it is easy to assemble several membrane units to scale up the useable membrane filtration surface from the laboratory-scale equipment (some cm^2) to industrial units with several hundred m^2 of membrane surface. At this operating level, filtration and membrane cleaning can be conducted in a continuous automated process with often efficient energy consumption; (3) membrane separation can operate in different process modes (continuous, batch, multi-stages) that can be also coupled with other technological unit operations.

Transport rate of species through the membrane (permeation) is achieved by applying a driving force across the membrane. The flow across the membrane can be driven by application of mechanical, chemical or electrical forces that can be hydrostatic or vapour pressure, concentration gradient, temperature or electrical potential. The way by which the material and the solution are transported across a membrane gives a broad classification of the separation membranes [77]:

- Pressure-driven processes, such as in microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO) or in gas separation (GS), or partial-pressure-driven processes, such as in pervaporation (PV)
- Concentration-gradient-driven processes, such as in dialysis
- Temperature-driven processes, such as in membrane distillation (MD)
- Electrical-potential-driven processes, such as in electrodialysis (ED)

Considering the temperature-sensitive biological activities of some water-extracted natural products, pressure-driven membrane processes are preferred for filtrating and concentrating such products. Depending on the membrane performances, often linked to the nominal membrane pore size, pressure-driven membrane separation process can be classified into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Their main characteristics are shown in Table 13.1.

Table 13.1 Classification and general characteristics of filtration membranes

Membrane uses	Microfiltration MF	Ultrafiltration UF	Nanofiltration NF	Reverse osmosis RO
Pore sizes	0.1–10 μm	1–100 nm	≤1 nm	<0.5 nm
	Porous membrane			Dense membrane
Osmotic pressure effect	Negligible	Very weak	Average to weak	Important
Specific transmembrane flux	100–1,500 $l \cdot h^{-1} \cdot m^{-2}$	40–200 $l \cdot h^{-1} \cdot m^{-2}$	50–100 $l \cdot h^{-1} \cdot m^{-2}$	10–60 $l \cdot h^{-1} \cdot m^{-2}$
Transmembrane pressure effect	Weak	Weak	Average	High
Usual operating pressure	0.1–3 bar	0.5–10 bar	4–20 bar	≥20 bar
Retention of →	Large size bacteria, yeast, particles	Bacteria, macromolecules, proteins, large size viruses	Viruses, 2-valent ions and molecules	Salts, small size organic molecules
Energy consumed	<0.5 kwh $\cdot m^{-3}$	<1 kwh $\cdot m^{-3}$	1–2 kwh $\cdot m^{-3}$	2–10 kwh $\cdot m^{-3}$

13.6.1.1 Microfiltration

When membrane filtration is used for the removal of larger particles, microfiltration and ultrafiltration are applied. Because of the open character (pores) of the membranes, the productivity is high, while the pressure difference applied between the membrane sides is low.

MF membranes are used for separation of particles with a size range of 0.1–10 μm (impurities, viruses and bacteria) from a solvent or a water-extract solution. The separation mechanism is based on a sieving effect of the membrane pores, and particles are separated according to their dimensions although some charge or adsorptive separation is possible. In MF process, the pressure applied is quite low ($P < 3$ bar) compared to that used in other filtration processes [78]. MF membranes were mainly used for sterilisation by filtration in the pharmaceutical industry (removal of microorganisms) or for final cleaning of rinse water in the semiconductor industry (removal of undesired particles). MF was also easily and economically used in cold sterilisation of beer and wine, as well as clarification of cider and other cloudy juices. Both organic and inorganic materials can be used for manufacturing microfiltration membranes. Most organic membranes are currently made of organic polymers (cellulose acetate, polysulfone or polyamide) whose qualities confer a great adaptability to different applications. Mineral membranes are totally made of a mineral matter (e.g. ceramic membrane), so they can be used within a large temperature range and a wide domain of mechanical constraints and even aggressive chemical media.

These membranes can be used according to the two main filtration configurations: cross-flow and dead-end filtration modes [79].

In the cross-flow filtration mode, the feed flow is tangential to the surface of membrane, the retained retentate is removed from the same membrane side, whereas the permeate flow, going through the membrane, is recovered on the other membrane side.

When using a dead-end filtration mode, all the fluid passes in a direction substantially perpendicular to the membrane surface, and all particles larger than the pore sizes of the membrane are stopped at its surface. The trapped particles prevent other contaminants from entering and passing through the membrane by building up a 'filter cake' on the surface of the membrane which reduces the efficiency of the filtration process until the filter cake is washed away in back flushing. The main disadvantage of a dead-end filtration is the extensive membrane fouling and concentration polarisation, and the process is a batch-type process which is easy to implement and usually cheaper than the cross-flow membrane filtration [80].

13.6.1.2 Ultrafiltration

UF membranes were firstly manufactured with the initial goal of producing high-flux RO membranes. The first commercial UF membranes were introduced in the mid-1960s by Millipore and Amicon (www.millipore.com) as a spin-off of the

development of asymmetric RO membranes. In the UF process, no significant osmotic pressure is generated across the UF membranes because of the membrane porous structure (pore size 1–100 nm) which allows permeation of micro-solutes (molecular weights < 300 Da) through the membranes [81]. UF membranes have an asymmetric porous structure and are often prepared by the phase-inversion process. UF membranes are used to retain macromolecules, colloids and solutes with molecular weight larger than 10,000. These chemical species may produce an osmotic pressure of only a few bar. Thus, the driving force in UF is mainly the hydrostatic pressure applied against one side of the membrane (0.5–10 bar). The selectivity of UF membranes depends on size and surface charge differences among compounds to be separated, on the membrane physical properties and on the hydrodynamic conditions applied.

13.6.1.3 Nanofiltration

The term nanofiltration was introduced by FilmTec (www.dowwaterandprocess.com) in the second half of the 1980s to describe a type of 'RO process' that allows some feed water ionic solutes to permeate selectively through the separation membrane, using a pressure gradient. NF spans the gap in particle size between UF and RO. The size of the solutes excluded in this process is of the order of 1 nm, while water and non-charged compounds with a molecular weight < 200 Da are able to permeate the semipermeable separation layer of the membrane. Different from RO membranes which have a non-porous structure and a transport mechanism of solution-diffusion, NF membranes operate at the interface of porous and non-porous membranes with both sieving and diffusion transport mechanisms. Therefore, it was acknowledged that NF performed an intermediate capability as 'loose' RO (non-porous, diffusion) or 'tight' UF (porous, sieving) [82, 83].

13.6.1.4 Reverse Osmosis

Reverse osmosis (RO) membranes do not work according to the principle of pores governing separations by microfiltration and ultrafiltration. Separation takes place by diffusion through the RO membrane. The pressure that is required to perform RO is much higher than the pressure required for MF and UF, while productivity is much lower.

Reverse osmosis (RO) is based on the diffusion principle and occurs when the water is moved across the membrane against the concentration gradient, from lower concentration to higher concentration. The principle of RO resulted from the application of a pressure against the opposing osmotic pressure generated by a solution containing solutes (Ps) to force the flow of water (Pw) in the opposite direction to the natural direction generated by the difference between osmotic pressures created by the two solutions (Ps > Pw). Pure water flows from the more

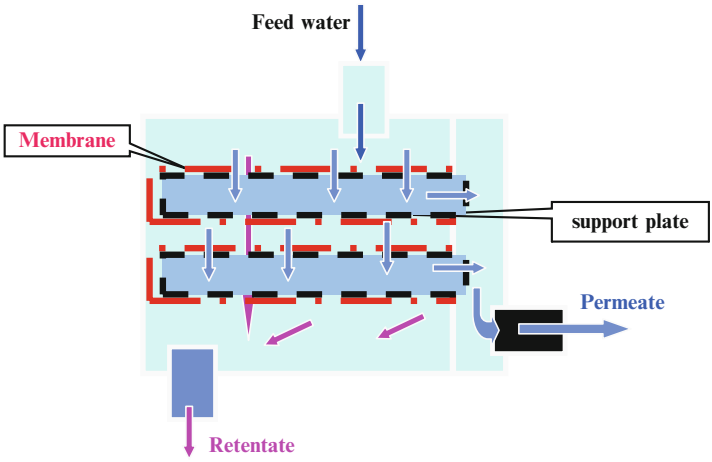

Fig. 13.23 Schema of a plate-and-frame module

concentrated to the less concentrated solution. RO is a membrane technology generally used to concentrate water extracts obtained from previous extraction techniques.

As RO membranes retained most of water-soluble compounds and salts, including the small monovalent ions, it is one of the methods used to desalinate seawater. RO membranes are generally categorised into asymmetric membranes and thin-film or composite membranes. An asymmetric RO membrane shows a multilayer structure made from one polymer material and has a thin, selective skin layer supported by a more porous sub-layer.

13.6.2 Typical Membrane Modules at Pilot Plant and Industrial Scales

Large membrane areas and small volumes are required for industrial applications in membrane processes. Membrane units set together into membrane modules are the practical solution. The module is the base for membrane installation and process design. Four main types of modules, depending on the supported membrane, can be distinguished as follows [84]:

- *Plate-and-frame module* is the oldest and simplest module. Sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other. In each feed and permeate compartment, a suitable spacer is placed. The number of sets needed for a given membrane area furnished with sealing rings and two end plates is then built up to a plate-and-frame stack. The membrane permeate is collected from each support plate, as shown in Fig. 13.23.

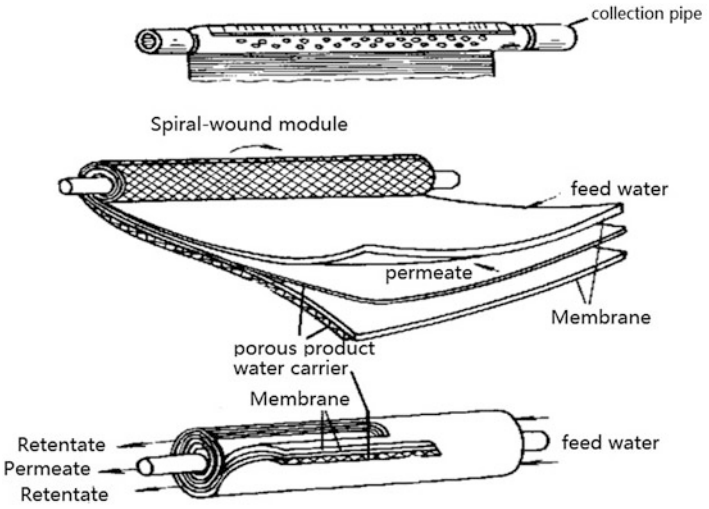

Fig. 13.24 Schema of a spiral-wound module

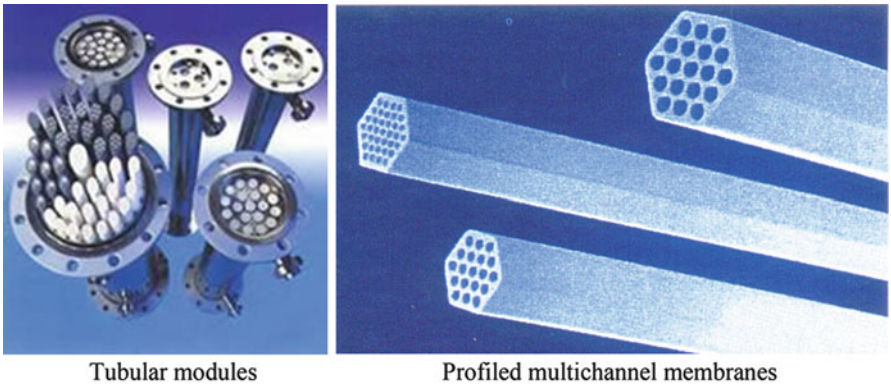

Fig. 13.25 Tubular filtration modules equipped with membranes and ceramic profiled membrane units

- *Spiral-wound module* is a rolled plate-and-frame module around a central collection pipe as shown in Fig. 13.24. Membrane and permeate-side spacer material are then glued along three edges to build a membrane envelope. The feed-side spacer separating the top layer of the two flat membranes acts also as a turbulence promoter. The feed flows axial through the cylindrical module parallel along the central pipe and the permeate flows radially towards the central pipe. The spiral-wound module has a compact structure and large membrane area per unit volume. It is easy to operate. The disadvantage is that the feed water must be clarified to prevent fouling.
- *Tubular module* is shown in Fig. 13.25. The feed solution always flows through the centre of the tubes, while the permeate flows through the porous supporting

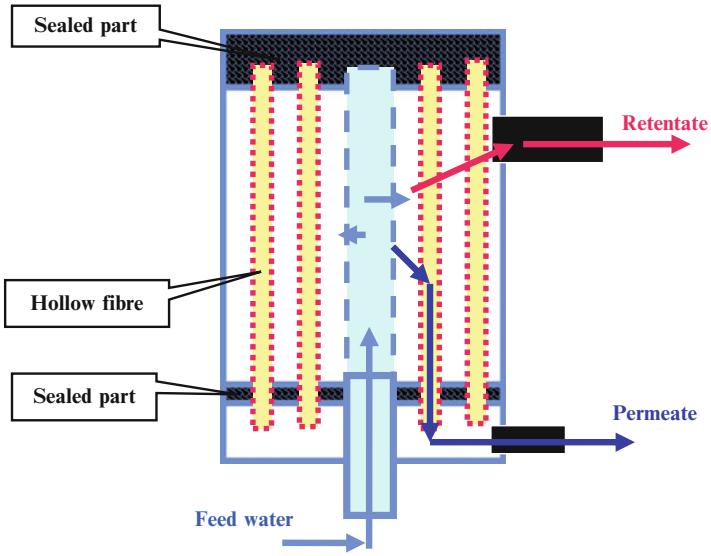

Fig. 13.26 Schema of a hollow-fibre filtration module

tube into the module housing. Profiled and multichannel ceramic membranes are mostly assembled in such tubular module configurations. The main advantages of the tubular module are usefulness and cleanness, but there is a major disadvantage for large energy consumers about its reduced exchange surface per unit volume (reduced compactness).

- *Hollow-fibre module* consists of a set of hollow fibres of diameter less than one micrometre assembled together in a module, as shown in Fig. 13.26. The free ends of the fibres are often potted with agents such as epoxy resins, polyurethanes or silicon rubber. The membranes are self-supporting for this module. This configuration provides the highest flow per module density.

The choice of the module configuration, as well as the arrangement of the modules in a system, depends on economic considerations with correct engineering parameters being employed to achieve this, which include the type of separation problem; the eases of cleaning, maintenance and operation; the compactness and scale of the system; and the possibility of membrane replacement [85].

13.6.3 Application of Membrane Technology at Pilot Scale

Perilla frutescens is an edible plant frequently used as one of the most popular spices and food colourants in some Asian countries such as China and Japan. Water extract of Perilla contains abundant polyphenols including anthocyanins, flavones

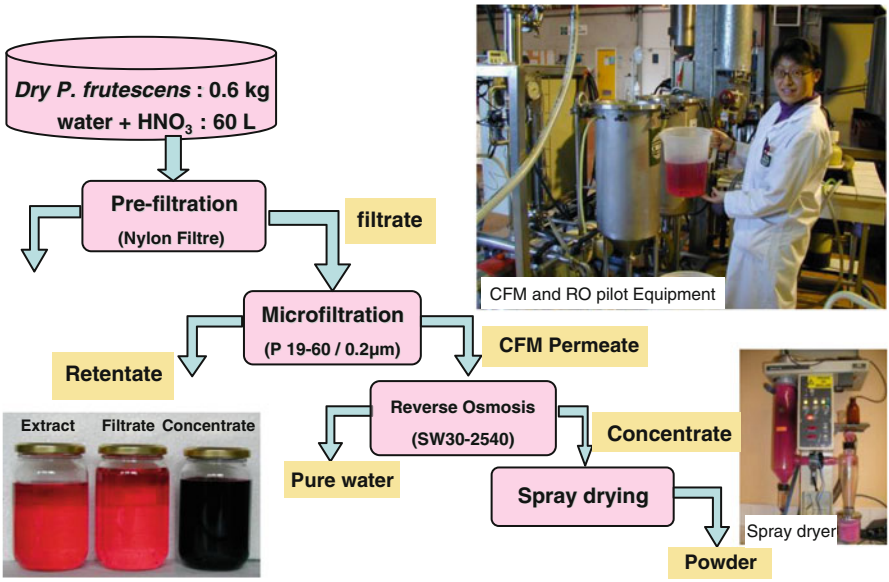

Fig. 13.27 The membrane process of perilla extracts production

and phenylpropanoids [86] that showed antioxidant activity [87]. Considering the heat sensibility of polyphenol compounds contained in this plant, especially anthocyanins, one of the natural colourants which can be used in food and pharmaceutical industry, the sterilisation and concentration of the water perilla extract should avoid the heat treatment. A membrane process including cross-flow microfiltration (CFM) and reverse osmosis (as shown in Fig. 13.27) was developed to clarify, sterilise and concentrate the perilla extract at pilot plant scale by Meng et al. [88].

The dry leaves of perilla were extracted by acidified water using a ratio of 1:100 (g/mL) in room temperature overnight. Then, the extract was pre-filtrated by a nylon cloth filter. After pre-filtration, a system of single-stage continuous feed and bleed loop configuration (TIA, Bollène, France) CFM was applied to clarify and sterilise the perilla extract. The multichannel ceramic membrane used was a *P* 19–60 (Membralox) industrial-type membrane, 800 mm long, 0.2 μm average pore size, with a total filtration surface of 0.304 m^2 (Pall-Exekia, Tarbes, France). The transmembrane pressure was set at 0.6 bar during the operation and the feed flow was controlled at 4.5 m/s. The CFM permeate flux stabilised rapidly after the start of the CFM to an average value of 150 L/h/m^2. The concentration of extract was realised by RO. The RO membrane used was of an industrial type, SW 30–2540 composite polymeric membrane, packed in a spiral-wound configuration (Filmtec), with 2 m^2 of filtration surface. The process was kept going at a constant transmembrane pressure of 40 bar until the volume of the RO retentate reached the value of the dead volume of the RO unit (3 L). The flux of the RO permeate (pure water) showed an immediate stabilisation at the value of 22 L/h/m^2 and stayed

constant at this level for more than 45 min of operation. Finally, the CFM permeate was concentrated 9.4 times by RO. HPLC analysis of the polyphenol compositions in the extracts (before and after concentration) showed CFM, and RO process did not make the degradation of the thermo-sensibility compounds. Finally, using a spray-dryer, the concentrated extract was totally dried and made into powder which was a stable antioxidant-active red product, with a long shelf-life.

The same general process chain was successfully applied to water extraction of different plant materials, including leaves and flowers from tropical trees, plants or herbs traditionally used in the local medicine. Therefore, concentrated water extracts have been prepared from vegetal material used by African traditional healers to prepare some local medicine or healthy beverage. Extraction-concentration process started with plant water diffusion followed by membrane purification–concentration. Membrane technology is used here for two purposes in the process: cleaning the extraction water before using it in the diffusion step and purifying the water extract (bacteria-free) and concentrating it for a better shelf-life in local conditions and for making local marketing easier than using a single-strength water extract.

Hibiscus sabdariffa flowers, *Delonix regia* flowers, *Justicia secunda* leaves and *Tectona grandis* leaves were some of the traditional African plants that have been processed with modern pilot-scale technology, in a way mimicking traditional preparation recipes delivered by local practitioners [89–91].

13.7 Conclusion

Although water is the 'best' and the safest solvent of the world, it was not yet applied usually in industrial extractions because of its low extraction efficiency towards many other non-water-soluble and valuable compounds that can be extracted from the worldwide biodiversity and the difficulty to concentrate water solutions. Many innovative technologies were developed to improve the efficiency of water extractions. Ultrasound-assisted extraction has already been applied in industrial processes such as the extraction of Chinese traditional medicine. Others technologies still remain operational only at the laboratory and pilot plant scales, and should need more research and development efforts to raise them to technically and economically viable applications for the industry. Regarding the problem of water-extract concentration, nanofiltration and reverse osmosis technologies may provide interesting alternative solutions depending on the value added to the water-extracted product and its potential uses in various industrial sectors, as a marketable finished product or as a raw ingredient for manufacturing others final products. With the additional use of membrane technologies in water extraction of various raw materials, the water-extracts can be eco-friendly concentrated at room temperature without extra-use of organic solvents or chemicals.

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