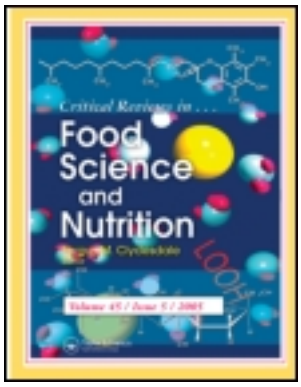

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Pretreatments for the Efficient Extraction of Bioactive Compounds from Plant-Based Biomaterials

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Pretreatments for the Efficient Extraction of Bioactive Compounds from Plant-Based Biomaterials

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The extraction of medicinal or functional compounds from herbal plants is an important unit operation in food and bio-industries. The target compounds are generally present inter- or intra-cellularly in an intricate microstructure formed by cells, intercellular spaces, capillaries, and pores. The major resistance of molecular diffusion in materials of plant origin always comes from the intact cell walls and adhering membranes. Therefore, increasing the permeability of cell walls and membranes plays a very important role to increase extraction yield and/or extraction rate.

Important pretreatment methods to modify the cellular structures and increase the permeability of cell walls or membranes are discussed in this paper. They include physical, biologic, and chemical treatments. In physical methods, mechanical disruption, high-pressure (HP) process, pulsed electric field (PEF) application, ultrasonic treatment, and freeze–thaw, and so on were applied. In biologic methods, different cell wall-degrading enzymes were applied to break-down cell walls or membranes and to diminish the overall internal resistance for transporting bioactive compounds from internal matrix to the external solution. In chemical methods, various chemicals for increasing the inner- or outer-membrane permeabilization were introduced. The principles of the technologies, examples of improvements, and advantages and disadvantages of the pretreatment methods are critically reviewed in this paper.

Keywords Pretreatment methods, physical treatment, pulsed electric field, ultrasound, freeze–thaw, enzymatic treatment, chemical treatment.

INTRODUCTION

Nutra-pharmaceuticals, and bioactive or functional compounds from natural products have been used as medicinal agents by human beings for thousands of years. There is no doubt that health-related product/process development has tremendous importance on the application of biofunctional materials in the food industry. Although some bioactive compounds can be chemically synthesized (Thuong and Asseline, 1985; Ortholand and Ganesan, 2004; Nikolaev et al., 2007), the extraction of compound-rich biomaterials from natural resources still play a very important role in current separation technologies because of the tremendous diversity in molecular structure, complexity of synthetic methodologies, or high cost of chemical synthesis technologies (Giri and Lakshmi, 2004; Guo, 2008; Larghi et al., 2009). Furthermore, the extraction of pharmaceutical compounds from natural materials, especially plant or animal origin, has attracted the attention of researchers and industries due to the increasing market demands. Thus, extraction technology with high-quality product, less energy consumption, and more environmental-friendly operation is highlighted by pharmaceutical/functional food and cosmetic industries.

Continuous and active attempts were made to improve the mass transfer during the crude extraction process. In industry,

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the most popular extraction method is solid–liquid extraction, which is an unsteady-state mass transfer of multi-components from a solid matrix to a solvent. Some novel extraction technologies to improve the extraction process have been developed continuously. These include supercritical fluid extraction (Mishra et al., 1993; Papamichail et al., 2000), microwave-assisted extraction (Camel, 2000; Pan et al., 2000), accelerated solvent extraction (Richter, 2000; Breithaupt, 2004), and ultrasound-assisted extraction (Vinatoru, 2001; Zhao et al., 2007). During the extraction process of solid–liquid system, extraction occurs at a rate expressed in terms of change in solute concentration in the solid matrix within a unit of time. In general, the transportation speed of solute through the solid matrix into the external solvent is a rate-controlling step. In order to maximize the yield of the novel extraction, a variety of pretreatments were used to increase cell wall permeability. At present, no comprehensive reviews on the pretreatment for effective extraction of bioactive components are available. In this review, we dealt with various pretreatment methods with principles of the technologies, examples of extraction improvement, as well as advantages and disadvantages of the technologies. The aforementioned pretreatment methods were divided into physical, biologic, and chemical means to introduce respectively. At the beginning, physics related to solid–liquid extraction was also introduced to understand the extraction process better with pretreatment.

FUNDAMENTAL PHYSICS BEHIND EXTRACTION

In general, biomaterials of plant origin contain an intricate microstructure including cells, intracellular spaces, capillaries, and pores as shown in Figure 1. The desired solute (i.e., bioactive compound) in the tissue may be present inter- or intracellularly. The molecules may pass through the space between two neighbor cells and the solute may be transported from the solid matrix to the exterior solvent phase. Alternatively, the solute may move through the capillaries in the solid matrix into the bulk external solvent. During extraction, turbulence is unlikely to occur in small capillaries and pores, leaving molecular diffusion as the main transport mechanism within the solid matrix. This so-called molecular diffusion is the process by which molecules are transported by random movements from a region of high concentration to that of lower concentration according to the concentration gradient (Equation (1), Simeonov et al., 1999).

$$\frac{\partial C_a(x,t)}{\partial t} = D_{\text{eff}} \frac{1}{x^\alpha} \frac{\partial}{\partial x} \left(x^\alpha \frac{\partial C_a(x,t)}{\partial x} \right) \tag{1}$$

where α can obtain 0, 1, and 2 associated with plate, cylindrical, and spherical geometries, respectively, and D_{eff} is the effective diffusivity in m^2s^{-1}.

After that, bioactive compounds inside the particles will move to the particle surface by diffusion in accordance with the concentration gradient inside the particles, and the bioactive compounds will be convected away to the extraction solvent. There should be a mass balance at the boundary as described in the equation (Izadifar and Baik, 2008):

$$-\rho_p D_{\text{eff}} \left. \frac{\partial C_{a\alpha}(t)}{\partial x} \right|_{\text{surface}} = \rho_{\text{sol}} h_m \left(C^* - C(t) \right)$$

$$= \rho_{\text{sol}}\, h_m \left(\frac{C_{a\alpha}(t)|_{\text{surface}}}{k} - C(t) \right) \tag{2}$$

where C^* represents equilibrium solute concentration at the interface in just the fluid phase, in kg kg^{-1}, h_m is the mass transfer coefficient in ms^{-1}, and k is the partition coefficient of target solute between solid phase and fluid phase at the interface.

The most important physical parameter that governs solid–liquid extraction speed is diffusivity of biocompound, D_{eff}. Thus, the most significant resistance barrier for the diffusion process are the cell walls and membranes of plant materials. Unlike animal cells, the plant cells have rigid and thick cell walls, where cellulose is the major component forming most of the supporting tissues and certain types of conducting cells. In cellulose, glucose monosaccharide units are combined by β-linkage formations that make the polymer straight and fibrous. They form microfibrils through hydrogen bonds and further fibrils. Moreover, cell walls are lignified to a different extent, further reducing the passage of molecules. For an efficient extraction process, it is important to make the cell wall permeable. By doing so, the effective diffusivity of the biocompound increases dramatically. A lot of research on increasing the permeability of cell wall has been done and, in this paper, we reviewed these methods under different categories as physical, biologic, and chemical methods.

PHYSICAL METHODS

Mechanical Disruption

Theoretically, the extraction time varies inversely with the square of the characteristic dimension of particles. The conventional method is to break down the cell walls of plant materials is by reducing the particle size (characteristic dimension). The cell wall can be disrupted with mechanical applications, such as cutting or grinding. Within a fixed unit mass of materials, the ruptured outer cells will also have a larger surface-to-volume ratio as particle size decreases. Thus, the extraction rate also increases with the surface area for mass convection.

Ma and colleagues (2009a, b) ground *Liuwei Dihuang*, a Chinese herb, to a particle size of 161.9 nm using a high-speed centrifuge sheering pulverizer. They found that the content of paeonol in extracts increased from 0.047 mg/g in microparticles

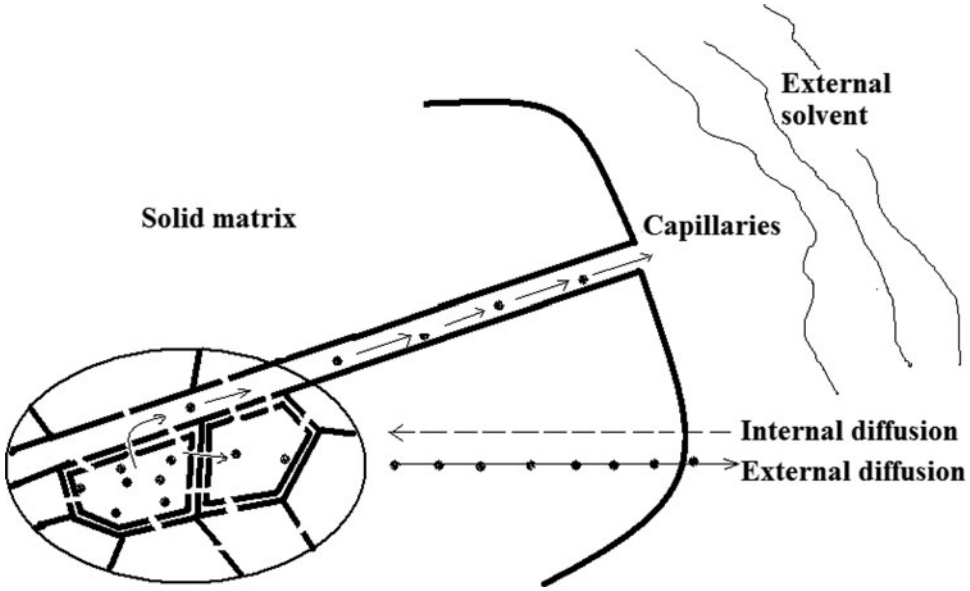

Figure 1 Scheme of the mass transfer in solvent extraction of solid food materials.

to 0.058 mg/g in nanoparticles, which indicated the extraction yield of paeonol jumped by 23.5% due to the breakdown of the plant cell walls.

However, size reduction is not always favored in the applications of extraction. When the particles are too small, it will bring a series of problems such as pressure drop in the extractor, slow drainage rates, contamination of fines in the extract, flow instability, and entrainment. Therefore, various novel treatment methods for cell wall breaking are introduced and discussed in the following content.

High-Pressure-Assisted Process

Principles and Mechanisms

Recently, the application of high-pressure technology, generally high hydrostatic pressure (HHP), to inactivate pathogens in preserving food has attracted great attention in the food industry. It is generally regarded as one of the promising emerging technologies to be adopted in the inactivation of vegetative microorganisms in the preservation of fruit juices, milk, seafood, and prepared meals without sacrificing the organoleptic and functional properties of treated products (Ashie and Simpson, 1996; Dogan and Erkmen, 2004; Jung and Mahfuz, 2009). Plant cell walls can also be ruptured by HHP treatment for efficient extraction.

In general, the high-pressure pretreatment process includes three steps: compression, holding at the desired pressure, and pressure release. All of the sample, pressure medium, and a vessel are fixed at an initial temperature at the beginning of the experiment. During the compression, pressure increases up to the desired pressure with a compressing fluid. The temperature normally increases by 2–3°C per 100 MPa as a result of the physical compression, depending on the composition of medium or food (Cheftel, 1995). There is no additional energy required during the holding phase, where the sample is kept under the same pressure for extended periods of time. When the pressure is not applied, the compression-induced temperature decreases to the initial value, resulting in volume expansion. Through this compression and expansion process, the application of HHP may bring about changes in the pressures inside and outside of the cell membrane, which pierces holes in membranes or cell walls.

Practical Issues for High-Pressure Treatment

It is known that sublethal injury of the membrane for microorganisms or cells are influenced by the application of pressure. Much work has been done on the inactivation of microorganisms, whereas there are limited reports that are discussed and observed on the plant or animal cells used widely in food industry. With larger cell sizes than the cells of microrganism, plant or animal cells can be broken down at lower levels of the applied pressure. Their effects and experimental conditions are listed in Table 1.

Corrales and colleagues (2009) reported an optimization of anthocyanin extraction from red grape skins assisted by HHP. Various levels at 200, 400, and 600 MPa of pressure were used in the experiment for finding the optimal anthocyanin extraction yield and strongest antioxidant activity. The highest antioxidant activity of the extracts at the optimum condition of 600 MPa and 30 minutes holding time were three-fold greater than that with the control extractions. In addition, the extraction yield achieved was 23% higher than control.

Compared with conventional solvent extraction, ultrasonic extraction, and heat-reflux extraction methods, the application of HHP most efficiently enhanced the extraction yield of caffeine

Table 1 The effect of high pressure on the soft plant cells

Plant tissues	Process conditions			Effects	References
	Pressure (MPa)	Processing time (minutes)	Temperature (°C)		
Red grape skin	200–600	30–90	20–70	Increased extraction yield (three-fold greater than control)	Corrales et al. (2009)
Green tea leaves	100–500	1–10	Room temperature	Much shorter extraction time than that of conventional extraction (20 hours to 1 minute)	Xi (2009)
Longan fruit pericarp	200–500	2.5–30	30–70	Doubled phenolic compound recovery	Prasad et al. (2010)
Panax quinquefolium L. (American ginseng) root	100–600	1–5	25	Much higher extraction yield (0.8661% to 0.661%) and shorter time (8 hours to 2 minutes) than that of heat reflux extraction.	Zhang et al. (2006)
Fresh carrots	100–550	2–30	20	Cell wall breakage as a result of the applied hydraulic pressure (50% loss in hardness)	Trejo Araya et al. (2007)
Rice endosperm cells	100–400	15–60	60	Enhanced cell permeability and, thus, facilitated the release of rice allergens	Aertsen et al. (2009).

from green tea leaves (Xi, 2009). The extraction yield obtained with the conventional method for 20 hours at room temperature was obtained by HPP at 500 MPa for only one minute. The holding time for the reaching equilibrium between intra- and extracellular solutions to achieve complete contact between bioactive components and the solvent was tested from one to ten minutes. The results showed that there was no significant increase in extraction yield with holding time, which indicated one minute was sufficient to achieve the equilibrium, which makes HHP methods energy efficient among the extraction methods.

High pressure was also applied to recover antioxidant and antityrosinase compounds from longan fruit pericarp (Prasad et al., 2010). The dried longan fruit pericarp powder (10 g) was mixed with 500 mL of 50% ethanol, and then pressurized for 30 minutes at 200, 300, 400, or 500 MPa, with dioctyl sebacate acting as the pressure-transmitting media. The highest total phenolic content obtained was 20.8 ± 1.9 mg/g at 500 MPa compared with 11.9 ± 1.2 mg/g for the control experiment. This indicated that high pressure increased phenolic compound recovery to approximately twice that of the control. Meanwhile, the highest total antioxidant activity of the extract was obtained at 500 MPa.

Zhang and colleagues (2006) developed a new method of ultrahigh-pressure extraction (UPE) to extract ginsenosides from *Panax quinquefolium L.* (American ginseng) root at room temperature. Different solvents, including water, ethanol, methanol, and *n*-butanol were used in the high-pressure extraction, and ethanol was shown to be the most efficient solvent. The yield of ginsenosides increased linearly with pressure in the range of 100–500 MPa. There was slight decrease in the extraction yield when the pressure was higher than 500 MPa. Under a pressure of 200 MPa, no obvious increase in the yield of ginsenosides was observed within a period of one to five minutes. The extraction yield of 0.861% ginsenoside-Rc in two minutes at 25°C 2as achieved by the UPE, which is much higher than that of 0.661% by heat-reflux extraction at 70°C for six hours. Therefore, UPE was proved to be the most efficient extraction method compared with the other methods.

Trejo-Araya and colleagues (2007) reported the effects of high-pressure processing on textural changes of fresh carrots, integrating microstructural and biochemical responses. Analysis of microscopic images provided insight into the mechanisms of textural changes, which included cell–deformation-related factors such as shape factor and elongation. Pectin solubilization and the release of low-molecular-weight uronides from cell walls can relate to the softening of plant tissue. At 20°C, hardness losses of 5%, 25%, and 50% were found for treatments at 100, 200, and 300 MPa, respectively. Textural changes of fresh carrot tissue were mainly associated with turgidity loss, a direct result of the applied hydraulic pressure. Therefore, the application of high pressure can increase the cell wall permeability, which facilitates the extraction process.

High pressure can also be used in cell destruction to create desirable functional properties. When endosperm cells present in rice grains were pressurized at 100–400 MPa, the partial destruction of endosperm cells enhanced their permeability to facilitate the preferential release of the major rice allergens (Aertsen et al., 2009).

Advantages and Disadvantages of High-Pressure Treatment

Compared with conventional treatment methods, HPP can be used as a promising tool either in fundamental research or in the development of new biotechnological applications. Within a very short process time, the high-pressure application can achieve a higher extraction yield on a commercial basis. The minimal thermal process conveyed by high pressure shows great potential for different industrial fields, from food to pharmaceutical applications. The HHP can be applied at room temperature successfully, and be regarded as a substitute technology for heat processing in microorganism inhibition. Furthermore, the high-pressure processing presents the advantage of its uniform and instantaneous application, which is independent to the size and shape of the treated products (Knorr, 1993). Although regarded as an environment-friendly, industrially-tested technology, high

pressure also has its drawbacks: limited application as a batch or semi-continuous process and high cost of pressure vessels. The pressure adoption may turn a raw product (such as fruit) to a paste rather than retaining its original shape because of the operative procedure: the first collapses by high compression and then suddenly expands when withdrawing the pressure. Therefore, the fruit products are pressurized as a "prepared product" rather than in their natural presentation (Guerrero-Beltrán et al., 2005).

Pulsed Electric Field Application

Principles and Mechanisms

Through a phenomenon called irreversible electroporation, PEF is a promising method with a high capability of increasing cell membrane permeability, by which it is possible to increase the extraction yield during the compression of plant tissues or solvent extraction. The application of a moderate electric fields (between 0.1 and 40 kV/cm for microseconds caused pores of limited size in cell membranes/walls to increase in their transmembrane potential. The cell pores generated by PEF treatment can be reversible or irreversible depending on the intensity of PEF treatment (Serpersu et al., 1985). For the reversible pores on the membrane, the viability of the cell is still maintained, pores generated by electrical strength will be resealed, and the permeability of membranes decreases to the original level when the electrical field is withdrawn. PEF receives a lot of attention, and a variety of work has been done on the microbial inactivation for pumpable liquid foods and beverages such as milk, pea soup, liquid egg yolk, green tea extracts, and red wine (Amiali et al., 2007; Zhao et al., 2008; Jaeger et al., 2009; Puértolas et al., 2010), as well as all kinds of juices including apple, orange, tomato, grape, mango, cranberry, etc (Jia et al., 1999; Liang et al., 2006; Marsellés-Fontanet and Martin-Belloso, 2007; Nguyen and Mittal, 2007; Evrendilek et al., 2008). Less work has been done on the use of electrical fields (PEF) for the modifications of the microstructure and texture of cells for solid foods.

Figure 2 shows a basic diagram of the PEF apparatus (Heinz et al., 2001). The main components of the PEF system are a high-voltage generator, charging capacitor, discharging switch, and application (or treatment) chamber. The generator provides high voltage with the help of a capacitor. The electrical energy is stored in the capacitor and the energy is released in the form of a high-voltage current to the samples between two electrodes for microseconds. For thermolabile bioactive compounds, a cooling device needs to be considered for application design due to potential heat generation during PEF treatment.

Practical Issues for PEF Treatment

The applied voltages are normally between 0.1 and 40 kV/cm depending on the purpose of the treatment. The critical transmembrane potential to induce membrane permeabilisation is

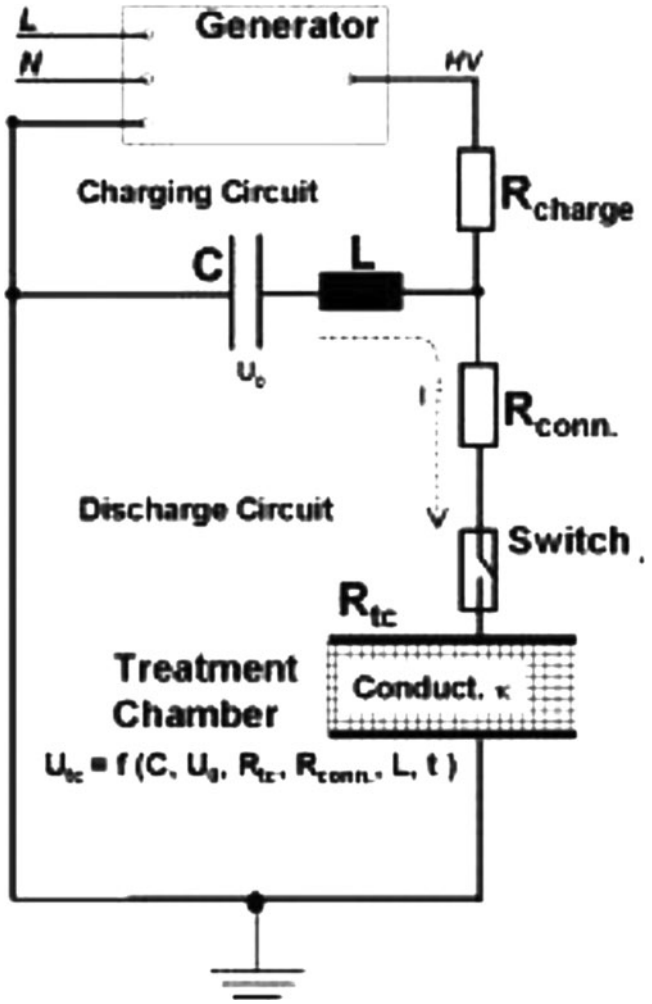

Figure 2 A schematic diagram of pulsed electric field application system (from Heinz et al., 2001)

dependent on the size and geometry of cells exposed in the electric field. The smaller the cells, the higher the field strength required. In general, the size of vegetable or animal cells, in the range of 40–200 μm, for food industry is greater than that of micro-organisms, in the range of 1–10 μm. Thus, the critical electric field strength for cell membrane plasmolysis for plant cells in approximately 1–2 kV/cm, which is much smaller than the 12–20 kV/cm required for microorganisms (Heinz et al., 2001).

Most food materials will not tolerate the low-intensity electric fields between 1 and 10 kV/cm, and their texture or microstructure will become altered under this range (Gudmundsson and Hafsteinsson, 2005). Their effects and experimental conditions are listed in Table 2.

Dörnenburg and Knorr (1993) investigated the application of PEF at a strength from 0 to 1.6 kV/cm on cultured plant tissues of *Morinda citrifolia* cells and examined its effect on cell permeabilization. The absence of distinct pigment release at 0.5 kV/cm showed that the cell permeability was not improved under this level of electric field for the system. In the extraction

Table 2 The effect of pulsed electric field on the soft plant cells

Plant tissues	Process conditions: Field strength (kV/cm)	Process conditions: Pulse duration (μs)	Process conditions: Pulse number	Effects	References
Morinda citrifolia cells	0–1.6	—	0–30	The cellular permeability was not improved under 0.5 kV/cm	Dörnenburg and Knorr (1993)
Beetroots	1	10	24, 54, 270	Low-level cellular damage occurred	Fincan et al. (2004)
Maize germ	0.6–7.3	280	120	Increase in oil yield (23.2% to 43.7%) and phytosterol content (785 mg/100 g to 1039 mg/100 g oil)	Guderjan et al. (2005)
Apple slices	0.2–2.2	10–100	1–100,000	Higher degree of cell destruction at a higher level of field strength	Lebovka et al. (2000)
Apple	0.-1	100	1000	Enhanced permeability and improved mass transfer (2.5×10^{-10} m^2/s to 3.9×10^{-10} m^2/s)	Jemai et al. (2002)
Beetroots	0–23.9	—	—	Improved the mass transfer (betanin concentration: 2.87 ppm to 3.04 ppm)	Kulshrestha and Sastry (2003)
Red beetroot	1–9	2–5	5–40	Five times higher extraction rate than control	Lopez et al. (2009)
Carrots	0–2.6	—	—	Enhanced juice yield (30% to 70.3%)	Knorr et al. (1994)

of pigment from beetroots (Fincan et al., 2004), low-intensity PEF treatment at 1 kV/cm with 270 rectangular pulses of 10 μs was applied. The extractability of pigments was shown to be approximately linearly proportional to the release of ionic species; therefore, the researchers inferred that relatively low levels of the cell damage occurred.

In a work by Guderjan and colleagues (2005), the effect of PEF treatment on dry milled maize on the extraction of phytosterol was observed in terms of cell disintegration index with different field strengths. The disintegration index steeply increased from 0 to 2 kV/cm; thereafter, the index change with field strength was not significant. It is interesting that the disintegration of cells was more severe (29.7%) at a field strength of 7.3 kV/cm, and the oil yield from maize germ did not increase accordingly. This indicated that the induction of stress reactions by a low PEF might stimulate metabolic activity and cause accumulation of secondary metabolites.

When the electrical field strength and/or treatment duration (such as number of pulses and pulse width) increases, a large pore is generated and persists even after the PEF treatment is terminated. Then reversible permeabilisation will progress to irreversible breakdown.

According to a report by Abidor and colleagues (1979), the electrical breakdown for cell membranes at a low electric strength (<0.2 kV/cm) and short duration (10^{-5}–10^{-6} s) was reversible, and the pores on the cell membranes could be recovered after cessation of the treatment. When the strength of the electric field was higher and the treatment duration was prolonged (0.5–2 kV/cm, 10^{-4}–10^{-5} s), the pores persisted on the cell membranes and the integrity of cells decreased.

Zimmermann et al. (1974) reported that reversible structural change of cell membranes occurred at an electric field strength of 1–10 kV/cm with a short pulse duration of 20 ns to 10 ms, whereas irreversible rupture occurred when pulse duration was prolonged to 10–15 ms (Zimmermann et al., 1976).

The impact of PEF at a field strength of 0.6–1.3 kV/cm and pulse duration of 280 μs was studied to examine its effect on the extraction of oils from olives, maize, and soybeans (Guderjan et al., 2005). Irreversibly disrupted cells result in a better and easier extraction/separation of food and biologic ingredients. The maize germ oil yield increased by 2.9% compared with untreated control. For extraction of phytosterol in the maize germ oil, the yield increased up to 14.7% higher with the PEF treatment.

Whether reversible or irreversible, the pores generated by PEF will promote the mass transfer of bio-compounds from the solid samples. Lebovka and colleagues (2000) established a simplified model to simulate the kinetics of dielectric breakage of cells from thin apple slices under PEF treatment at field strengths of 0.2–2.2 kV/cm and pulse duration of 10–100 μs. The proposed model included a "jamming" behavior, which was consistent with the experimental observations. The effect of electric treatment was more efficient at higher levels of field strength because of the associated higher degree of cell destruction.

The effect of low PEF (0.1–1 kV/cm) on the diffusion characteristics of soluble substances from apple slices was investigated (Jemai et al., 2002). The diffusion coefficient of soluble substances was reported to increase after the application of the electrical field. The enhancement of diffusion coefficient was detected with the intensities of 0.1–0.15 kV/cm at 20°C and 75°C. At an electrical intensity of 0.5 kV/cm and 100 μs duration, the diffusion coefficient was 3.9×10^{-10} m^2/s at 20°C for the PEF-treated sample, which was higher than the value of 2.5×10^{-10} m^2/s for untreated samples. In addition, the diffusion coefficient was 13.4×10^{-10} m^2/s with PEF treatment, compared with 10.2×10^{-10} m^2/s for thermally denatured samples at 75°C. The result indicated that PEF treatment increased permeability through the apple tissue and improved mass transfer.

In a report by Kulshrestha and Sastry's (2003), the optimum mass transfer increase of beet dye from beet roots was obtained at a field strength of 10–20 V/cm. Reflecting the cell membrane damage, the concentration of betanin was 3.04 ppm with PEF, higher than the 2.87 ppm with conventional extraction. When the

electrical strength was les than 5 V/cm, no distinct enhancement was detected.

Lopez et al. (2009) tested the effect of PEF on betanine extraction from red beetroot. Thin disc samples were treated with 5 pulses and 1–9 kV/cm (corresponding specific energies of 0.02–0.70 kJ/kg). With 5 pulses at 7 kV/cm, they found approximately 90% of total betanine was released after 300 minutes of extraction, and the extraction rate was five times higher than that of non-treated samples.

With PEF pretreatment of carrots, apples, and coconuts, there were significant increases by 10–40% in the yield of their juices and coconut milks (Gudmundsson and Hafsteinsson, 2005). For carrot processing for the coarse particles (∼3.0 mm), the maximum juice yield of the control was 30%, whereas the yield increased to 70.3% when PEF treatment was applied. For fine particles (∼1.5 mm), the PEF treatment raised the extraction yield from 51.3% to 76.1% (Knorr et al., 1994).

Advantages and Disadvantages of PEF Treatment

The low energy consumption, short processing time, and moderate temperature make PEF treatment a potential means to improve the extractability of valuable bioactive compounds from different food matrices at an industrial scale (Praporscic et al., 2007). In addition, the application of low-intensity PEF may be notable to separate valuable compounds from metabolically active tissues at higher energy efficiency. The high-intensity PEF treatment can be a promising alternative to produce fresher and safe pasteurized liquid foods than conventional heat treatments.

However, the disadvantages of PEF technology, such as non-uniform distribution of field strength which is an intrinsic characteristic of technology and limited selection pool of solvents with PEF, might slightly reduce the feasibility of this method in some industrial applications. Further investigation of the effect of PEF operating parameters on the extraction of bioactive compounds needs to be extensively carried out.

Ultrasound Irradiation

Principles and Mechanisms

Ultrasound has a frequency higher than 20 kHz (Mason, 1990). It is another tool which can be effectively used to make cell walls of plant based biomaterials more permeable to the solute. Unlike electromagnetic waves, sound waves must travel in matter because sound waves are mechanical vibrations. When passing through matters, sound waves impose expansion and compression cycles on the medium. In a liquid, if the ultrasound frequency is sufficiently high, the expansion cycle causes localized negative pressure. When the local negative pressure exceeds the tensile strength, bubbles or cavities are formed in the liquid. In a liquid–solid (biomaterial) system, adjacent to the solid boundary, the shape of cavity during collapse is asymmetric and high-speed jets of liquid are produced when bubbles are collapsed. The whole process from cavity formation to cavity collapse takes place within a very short time period, which may generate a powerful liquid jet when the cavity is closed to a solid surface. This asymmetric implosion-induced liquid jet moves through the bubbles to the surface at the speed of 400 km/h (Stephanis et al., 1997). The influence of the jets on the solid surface is so strong that serious damage to the solid surface is made. It is shown that ultrasonically induced cavitation will increase the permeability of the plant tissues. The rupture of cell walls identified by scanning electron microscopy in soybean (Li et al., 2004) and *Radix Bupleuri* (Zhao et al., 2007) proved the mechanical breakdown by ultrasound and explained the increase in extraction yield to have occurred as a result of greater release of desired content from the solid matrices.

The apparatus of ultrasound treatment can be designed as a bath or probe. The process can be also designed to be online or in a batch. The important operating parameters during ultrasonic treatment are operating temperature, duration of sonication and power, probe shape, vessel geometry, and process type (continuous or batch). To obtain the best extraction yield, the ultrasonic wave distribution inside an extractor is also a key parameter. The maximum sonication power is observed in the vicinity of the radiating surface of the ultrasonic horn. As the distance from a radiating point increases, the ultrasonic intensity decreases abruptly. The presence of solid particles also attenuates the ultrasonic intensity (Romdhane et al., 1995). The effect of ultrasound on extraction yield and kinetics also varies with the nature of the plant material to be extracted.

Practical Issues for Ultrasonic Treatment

Many reports of ultrasound-assisted extraction have been widely published, whereas only a limited number of reports on ultrasonic pretreatment has been summarized and published. Table 3 outlined more details in the application of ultrasound as an effective pretreatment method prior to the extraction process.

Jiménez et al. (2007) investigated the effect of high-power ultrasonic pretreatment for virgin olive oil extraction from olive paste. There were two treatments of ultrasound in the experiment: the direct sonication by a probe horn at an intensity of 105 W/cm^2 and frequency of 24 kHz, and indirect sonication in an ultrasound-cleaning bath at 150 W/cm^2 and 25 kHz. Direct sonication achieved a better oil extractability with high moisture content (>50%) of olive paste, whereas indirect sonication resulted in greater extractability with low-moisture (<50%) olive fruits. According to the experimental result, the better product quality of extracted oils including lower bitterness and higher content of tocopherols, chlorophylls, and carotenoids was obtained from sonicated pastes.

Shah et al. (2005) applied ultrasound as a pretreatment method before aqueous oil extraction from the seeds of *Jatropha curcas* L. The ultrasound-assisted extraction provided 67% (w/w) of oil yield after ten minutes of sonication in an alkaline medium. In addition, an extraction yield of 74% was obtained by ultrasonic irradiation for five minutes followed by

Table 3 The effect of ultrasound as a pretreatment method on food materials

Plant tissues	Process conditions: Frequency (kHz)	Process conditions: Processing time (minutes)	Process conditions: Temperature (°C)	Dissipated power (Watt)	Effects	References
Olive paste	24 or 25,	0–30	20–35	—	Better properties of extracted oils (bitterness: 4.0 to 2.4).	Jiménez et al. (2007)
Seeds of *Jatropha curcas* L	42	5–15	37–50	—	Shorten the process time (18 to six hours).	Shah et al. (2005)
Almond and apricot seed	42	2.5–15	40	—	Increased oil yields (75% to 95%) and shorter extraction time (18 to six hours)	Sharma and Gupta (2006)
Corn slurry	20	1/3–2/3	10	Low: 274 ± 5 High: 475 ± 15	20-fold decrease in the corn particle size and three-fold increase in the glucose-release rate	Khanal et al. (2007)
Defatted soy flakes	20	0.25–2	4	Very low: 154 ± 1.5 High: 1280 ± 21	Broke the cell walls, and reduced particle size approximtelyten-fold.	Karki et al. (2010)

aqueous enzymatic oil extraction. The processing period was shortened from 18 to six hours with ultrasonic pretreatment. The positive effect of pretreatment by ultrasound in the aqueous enzymatic oil extraction from almond and apricot seed was also confirmed (Sharma and Gupta, 2006). Compared with the 75% (w/w) oil yield at 40°C for 18-hour treatment by aqueous enzymatic oil extraction from almond seeds, the application of 70 W ultrasound for 2 minutes increased the extraction yield to 95% in only six hours. The scanning electron micrograph (SEM) image visually proved the disruption of cell walls by application of ultrasound. A similar result was obtained in oil extraction from apricot seeds.

In addition, high-power ultrasound was also adopted in the treatment of corn slurry to increase liquefaction and saccharification for ethanol production (Khanal et al., 2007). The corn slurry samples were pretreated by ultrasound for 20 and 40 seconds at amplitudes of vibration ranging from 180 to 299 μm_{pp} (peak-to-peak amplitude in micrometers), followed by enzymatic reaction converting the cornstarch into glucose. Compared with the untreated sample, the corn particle size decreased approximately 20-fold after the ultrasonic treatment, and the cell walls of the corn were ruptured as seen on SEMs. The glucose-release rate increased as much as three times for sonicated samples compared with the control group.

For the defatted soy flakes, ultrasonic pretreatment prior to the extraction facilitates the release of protein and sugar from the solid matrix (Karki et al., 2010). The ultrasonic waves at high amplitude for 120 seconds provided the highest increase in yield of 50% for total sugar and 46% for protein. The ultrasonic treatment only broke the cell walls identified by SEM images, which also reduced particle size approximately 10-fold in comparison with the untreated sample. The new surface explosion generated in the medium solvent also increased the contact of protein and sugar with the solvent, which accelerated the rate of extraction and increased the extraction yield. The result showed that ultrasonic treatment application can also reduce the overall cost of producing soy protein from flakes.

In recent years, the application of high-power ultrasound to increase the biodegradability of the sludge as an emerging pretreatment method has received more attention (Pilli et al., 2010). Ultrasonication has been proved to be a very effective mechanical method to enhance the sludge digestibility by disrupting the properties of the sludge, which is very relevant to the treatment of sewage sludge in all wastewater treatment plants. The sonication parameters and sludge characteristics determine the degree of disintegration of sludge. The optimum parameters for the best effect vary with sludge characteristics and the ultrasonication reactor system.

Advantages and Disadvantages of Ultrasonic Treatment

High-power ultrasound has been widely used in the food industry for its low cost on apparatus, simple operation, and effectiveness in increasing yield. The application of ultrasound promotes the extraction yield and accelerates the rate of extraction in solid–liquid extraction. It can also reduce the temperature and time of operation, which is specially preferred for the extraction of the thermoliable compounds. Compared with other techniques such as high-pressure application, the ultrasound apparatus is much cheaper and easier to operate. The energy consumption was less in the domain of ultrasound pretreatment. On the basis of the report by Zhang and colleagues (2011), ultrasound seems to be considered as an energy-efficient technique in silica gel regeneration at low temperatures. Under experimental conditions of 35°C and moisture ratio in the range of 0.15–0.3 at dry basis, the total specific energy consumption was 38–40 MJ/kg and 18–20 MJ/kg for conventional thermal regeneration and ultrasonic treatment at 60 W, respectively. The lowest total specific energy consumption was achieved at 55°C and 60 W. Furthermore, unlike PEF, there is no restriction of the solvent type in the extraction, which expands its application to a wide variety of natural compounds.

However, the effectiveness of ultrasound associates closely with the nature of products and the extraction system. The

ultrasonic wave may be attenuated by the shape of the extractor or presence of solid particles. The distribution of the ultrasonic wave is non-uniform and restricted to the area in the vicinity of the ultrasound probe, which brings a challenge to its application on a very large industrial scale.

Freeze–Thaw Process

Principles and Mechanisms

Takamatsu and Kumagae (2002) demonstrated that biological cells may be injured not only by chemical damages but also by mechanical damages, which are caused by ice crystal compression. The freezing rate can be adjusted such that relatively large ice crystals grow in the biological material. Griffiths and colleagues (1979) investigated Chinese hamster ovary (CHO) cell size during the cooling, warming, and post-thawing periods of the freeze–thaw cycle. The cells were cooled at 1°C/min or 200°C/min and subsequently thawed, and their structural change was studied with a cryomicroscope. The cells shrank significantly and no intracellular ice appeared at a cooling rate of 1°C/min, whereas partial intracellular ice formation occurred and cells containing the most ice shrank least at a cooling rate of 200°C/min. In the thawing process, the cells swelled and their size was larger than that of non-frozen controls at a slow cooling rate and cells containing intracellular ice swelled to a greater extent at a fast cooling rate.

Where the freezing rate is not fast, the number of ice crystals will be small but are large in size. These large crystals bring about alteration of the plasma membrane due to mechanical compression, and the cells may not tolerate subsequent swelling, thus leading to cell damage during the thawing process. It is believed that the elevated concentration of extracellular solute is the main cause of the cellular injury. However, the investigation of membrane alteration and damage at the microscale level still needs to be further conducted (Takamatsu and Zawlodzka, 2006). Drying evacuates the water from such damaged biomaterials and can induce more fine pores within the product. The desired solute will be promoted to release from the solid particles because of the cell rupture by the freeze–thawing process.

Therefore, the freeze–thaw process can be considered as an approach to damage biological cell walls by mechanical compression.

Practical Issues for the Freeze–Thawing Treatment

Fresh fruits and vegetables contain more water and their cell walls are less elastic than the cell membranes of animal cells (Mohsenin, 1986), which makes it easier to form large ice crystal and cause inevitable cell damage in the freezing process.

Modise (2008) investigated the effects of various freezing and thawing treatments on the volatile profile of strawberries. Freezing was carried out at −20°C or −80°C or by rapid freezing in liquid nitrogen (−196°C). After one night or a week, berries were later left to thaw at room temperature for natural thawing, and some were forced-thawed in a 30°C water bath. In the extraction process, the concentration of most esters such as hexyl acetate, ethyl methyl hexanoate, and methyl acetate were increased significantly by week-long freeze–thaw treatment in comparison with fresh berries. It was found that more acetaldehyde compounds exist in forced-thawed berries than naturally thawed samples.

Oszmiański and colleagues (2009) studied the stability of phenolic compounds of strawberry cultivars at various freezing and thawing conditions. Between 4.5% and 33.6% of polyphenols were lost after the prefreezing treatment. In the thawing process, the force-thawed strawberries in a microwave oven had a further positive effect on retention of (+)-catechin and ellagic acid, in comparison with the natural thawing process at 20°C for 20 hours.

Advantages and Disadvantages of Freeze-Drying Treatment

The freeze–thaw process provides a clean alternative to break the cell walls to improve the extraction yield in food-extraction processes. After the pretreatment, there is a minimal change in color or flavor, and it retains most of the nutrients. With the increasing concern about food quality, this process could be considered a valuable alternative to pretreat the food for better quality in the extraction of valuable compounds from food materials.

At present, this freeze–thaw process is not widely used for pretreatment in the food industry due to its high operating costs and long processing time.

BIOLOGICAL METHODS

Principles and Mechanisms

Most of the plant cell walls contain approximately 10% protein and the other large portion is made of polysaccharides, including cellulose, hemicellulose, and pectin (McNeil et al., 1984). The component composition of polysaccharides varies with the variety of the raw plant materials. For example, the proportion of polysaccharides is 22% for cellulose, 29% for semicellulose, and 39% for pectin in rapeseeds (Domínguez et al., 1994). However, there is approximately 30% cellulose, 30% hemicellulose, and 35% pectin in grasses (Carpita, 1996; Cosgrove, 2007). The enzymes which hydrolyze these components can be used to improve extraction of the biocomponent inside the plant materials as a pretreatment. By disintegrating the cell wall with enzymatic reaction, the increased permeability of the cell wall will enhance the extractability of desired solute from the broken cells.

The important parameters which should be considered for the enzyme treatment are reaction time, temperature, pH, particle size of raw material, and type and concentration of enzyme. The

optimum temperature for the treatment is related to the thermal kinetics of molecular movement and protein denaturation. Normally, the optimum temperature lies between 35°C and 65°C in the enzymatic pretreatment for extraction of oils from fruits and oilseeds (Domínguez et al., 1994).

Practical Issues for Enzymatic Treatment

One of the important applications of an enzymatic pretreatment is to increase the yield of edible oil from fruits and oilseeds. Domínguez and colleagues (1994) summarized the enzymatic pretreatment for oil extraction from olive, avocado, coconut, sunflower, soybean, rapeseed, palm, etc. The effects of reaction time, temperature, pH, particle size, dilute ratio, centrifuge speed, and enzyme concentration have been compared. It was shown that the effect of enzymatic pretreatment was significant on the oil extraction yield. High-quality oil was extracted and not influenced by the type of enzymatic reaction. However, the enzymatic reaction depended on the characteristic of seeds and the shape of cultivar. The extraction yield of oil from grape seeds increased 106% after the enzymatic treatment, compared with non-treated samples (Passos et al., 2009). With the prolonged reaction time with enzyme from 24 to 120 hours, the extraction yield increased from 13.7% to 17.5%, which presented 163% increment to those samples without enzymatic pretreatment.

The enzymatic reaction can be also applied to break cells in the fruits and promote juice production. An enzyme cocktail of pectinases and cellulases has been reported to give a juice yield up to 100% (Alkorta et al., 1998). The function of various types of pectinases in the fruit juice production was discussed previously (Kashyap et al., 2001). The cloudiness and bitterness of fruit juices can be reduced by adding acidic pectinases originating from fungal sources, especially *Aspergillus niger*. Alkaline pectinases, mainly from *Bacillus* spp., were generally used in the pretreatment of pectic wastewater from fruit juice industries, and in the textile industry for the retting and degumming of fiber crops.

Advantages and Disadvantages of Enzymatic Treatment

Enzymatic pretreatment can be done effectively at moderate temperature (Domínguez et al., 1994). The method needs no specific requirement of apparatus and can be used in continuous production at industrial scale. Enzymatic reaction can occur in mild conditions, which is preferred from the view point of energy saving. After the enzymatic reaction finishes, parts of cell walls are disintegrated, leaving a primary frame without considerable chemical contamination. The quality of extracts, such as oil, will not be affected by adding enzyme in the system, making enzymatic pretreatment a clean, pollution-controlled, safe method.

The main disadvantage of the enzymatic pretreatment is the sensitive properties of enzymes. The enzymatic reaction will be affected by various conditions, not only by pH and temperature, but also the characteristic of raw materials, solvent, environment, etc. Some enzymes are expensive or unstable to the environment. All of these need to be further developed or improved in the practical application of enzymatic treatment.

CHEMICAL METHODS

Principles and Mechanisms

As previously mentioned, the major components in cell walls are polysaccharides, which are also targeted as sugar sources for biofuel production. Through various chemical pretreatments, such as acid and alkaline hydrolysis, the molecular structure of cell walls may be degraded. The effects of chemical treatments for cellulose microfibrils isolated from banana rachis were evaluated by means of SEM, ion chromatography, Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), TEM, and electron and X-ray diffraction (Zuluaga et al., 2009). The morphology and structure of the SEM images of treated samples showed that constituents such as pectins and hemicelluloses were hydrolyzed by the action of alkaline solutions, whereas the removal of lignin needed additional steps of sodium chloride or hydrogen peroxide treatment. Acid was applied as a catalyst to break down heterocyclic ether bonds between sugar monomers in the polymeric chains, which are formed by hemicellulose and cellulose (Laopaiboon et al., 2010). By changing the molecular structure of the lignin with chemicals, cellulose and/or hemicellulose will be more accessible for further processing. Ozone and peroxide can also be used in oxidation and reaction with organic compounds by attacking the cell walls and outer membrane, especially for bacteria, which may cause cell damage.

Practical Issues for Chemical Treatment

Chemical pretreatment, by using acids, alkali, or organic solvents, has been widely used to cleanse cellulose of lignin and hemicellulose in the natural fiber or for textile treatment (Thomsen et al., 2006). The effects of chemical pretreatment for the plant tissues are listed in Table 4.

Sun et al. (1995) investigated the effects of alkaline and oxidizing agents as pretreatments of wheat straw at various temperatures and exposure times. Sixty percent and 80% of lignin and hemicellulose were released through delignification and dissolution with the pretreatment of 1.5% sodium hydroxide (NaOH) for 144 hours at 20°C.

Yamashita et al. (2010) also used sodium hydroxide as a pretreatment to enhance the digestibility of the holocellulose

Table 4 Chemical pretreatment of plant tissues

Plant tissues	Process conditions			Effects	References
	Chemicals	Processing time (hours)	Temperature (°C)		
Wheat straw	H_2O_2, NH_4OH, $Ca(OH)_2$, KOH, LiOH, NaOH,	0.5–144	0–80	Effective delignification with the pretreatment of 1.5% NaOH (80% hemicellulose removed)	Sun et al. (1995)
Bamboo	NaOH, H_2O_2	1	90 & 121	Enhanced the digestibility of the cellulose (84.3% to 90.1%)	Yamashita et al. (2010)
Sugarcane bagasse	NH_4OH, HCl, H_2SO_4	1–5	90–120	Obtained the optimal catalytic efficiency (up to 10.85%) with 0.5% of HCl at 100°C	Laopaiboon et al. (2010)
Cotton stalks	H_2SO_4, NaOH, H_2O_2, O_3	0.5–1.5	4, 90 & 121	Sodium hydroxide pretreatment resulted in higher cellulose conversion than acid pretreatment (60.8% to 23.85%).	Silverstein et al. (2007)

component in bamboo. Holocellulose components are covered with the rigid lignin in bamboo cells. Because of the poor accessibility of enzyme and digestibility of these holocellulose components, pretreatment to degrade or remove the rigid lignin is necessary to promote the production of sugars by enzymatic saccharification. Through the pretreatment of 20 atm steam explosion and 10 wt.% sodium hydroxide treatment at 121°C, maximum value of glucose production, with 456 mg/(g initial dry sample) of glucose and 460 mg/(g initial dry sample) of reducing sugar, was obtained. However, the pretreatment of combining 1% (v/v) hydrogen peroxide and 1 wt.% sodium hydroxide at 90°C for 60 minutes also introduced as much as 399 mg/(g initial dry sample) glucose and 568 mg/(g initial dry sample) reducing sugar production without severe conditions of high pressure and temperature for steam explosion. It was shown that alkaline peroxide pretreatment was an effective and environment-friendly method for the enzyme saccharification of bamboo.

The acid hydrolysis of sugarcane bagasse for lactic acid production was studied by Laopaiboon and colleagues (2010). In their work, the lignin was first removed by ammonium hydroxide (NH_4OH), and then the remaining solid was hydrolysed by 0.5%, 2%, 3%, and 5% (v/v) of hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) across a range of reaction times (one to five hours) and incubation temperatures (90–120°C). The optimal catalytic efficiency could be obtained with pretreatment of 0.5% of HCl at 100°C for five hours, on 89% xylose as the main fermentable sugar in the hydrolysate.

Silverstein and colleagues (2007) compared the effectiveness of various chemical pretreatments on the saccharification of cotton stalks to ethanol. The pretreatment methods include H_2SO_4, sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and ozone (O_3) treatment. There was a positive linear relationship between xylan solubilization and pretreatment severity. The pretreatment with sulfuric acid at 2% at 121°C/15 psi for 90 minutes, resulted in substantial solubility of xylan up to 95.23% in cotton stalks, but the cellulose to glucose conversion was lowest at 23.85%. Delignification was the most significant effect of sodium hydroxide pretreatment. The highest level of delignification of 65.63% was achieved with 2% NaOH treatment at 121°C/15 psi for 90 minutes. In addition, sodium hydroxide pretreatment showed higher cellulose conversion at 60.8%. However, hydrogen peroxide pretreatment resulted in lower lignin and xylan solubilization than expected. Moreover, 29.51% delignification and 49.8% cellulose conversion were obtained with 2% hydrogen peroxide pretreatment at 121°C/15 psi for 30 minutes. The decomposition of hydrogen peroxide to water at high temperatures may reduce the effect of pretreatment. Unexpectedly, ozone did not cause any significant changes in lignin, xylan, or glucan contents over time. Possible explanations include insufficient time, low ozone concentration, or uneven distribution of ozone throughout the sample. In other works (Sakai et al., 1997; Tanaka et al., 1997), the barely degradable compounds can be transferred into more easily degradable ones in the digestion of waste-activated sludge using ozone, acids, or alkali as the chemical pretreatment.

Advantages and Disadvantages of Chemical Treatment

The merit of easy operation, cheap and abundant source of chemicals, and effectiveness in cellulose or lignin degradation has made chemical pretreatment a conventional method to make cell walls more accessible for further degradation. However, chemical pretreatments also have serious disadvantages: specialized corrosion-resistant equipment is required; the chemical wastes will exist in the system and cause contamination; additional washing and separation to remove the chemicals needs to be included and makes the process more complicated.

OTHER POSSIBLE METHODS

The steam explosion treatment is a well-known method of disrupting various lignocellulosic plant materials into cellulose, hemicellulose, and lignin (Saddler et al., 1993). At a high pressure and temperature, steam was used to hydrolyze the cell walls components in plant materials. Then a sudden reduction of the pressure for the hydrolyzed products led to the generation of

low-molecular weight substances from highly lignocellulosic biomass (Vignon et al., 1995). Chemical effects and mechanical forces are combined in this pretreatment. The formation of acetic acid from acetyl groups present in hemicellulose was promoted by the hydrolysis (autohydrolysis) at high temperatures. The explosive decompression of pressure causes mechanical effects on fibers and facilitates the production of small molecular compounds. Reports have shown that steam explosion can be recognized as one of the most efficient pretreatments for hardwood and agricultural residues (Excoffier et al., 1991; Moniruzzaman, 1995), while it is less effective for softwoods (Clark and Mackie, 1987). Similar to the steam explosion pretreatment, ammonia/CO_2 explosion is another type of physicochemical pretreatment for lignocellulosic materials, such as recycled paper mix, sugarcane bagasse, barley straw, corn stover, and rice straw (Vlasenko et al., 1997; Zheng et al., 1998). However, the application of high pressure and temperature in these methods increases the requirement of specific equipment and cost of operation.

Microwave (MW) dielectric heating is widely applied in the food industry because of its high energy efficiency and short processing time. Different from the conventional heating method, microwave heats the whole sample simultaneously by absorbing and converting MW energy directly into heat. Weak hydrogen bonds can be disrupted through the promotion of the rotation of molecular dipoles such as water with an alternating (2450 million times/second) electric field. Microwaves can heat wet biomaterials quickly, resulting in the occurrence of steam explosion when the stream pressure development by microwave irradiation is faster than pressure release to the exterior of the cells. The movements of dissolved ions also enlarge solvent penetration into the matrix and, thus, facilitate the desired solute dissolved into the solvent. Ooshima and colleagues (1984) showed that MW treatment played a positive role in biomass digestion and greatly increased the accessibility of the cellulose materials. Ma and colleagues (2009) also reported that silicified waxy surface of rice straw was disrupted by MW pretreatment through the chemical composition analysis. The application of MW resulted in the breakage of lignin–hemicellulose complex and partially removal of silicon and lignin. Microwave has been widely applied in the extraction of bioactive compounds from the natural materials, with its advantages in terms of less requirement of solvent, shorter process time, better products, and lower costs.

Radio frequency (RF) heating is also an emerging heating technology which provides uniform volumetric internal heat generation within particles placed between its two electrodes. Different from MW, RF has larger penetration depth, up to several meters, into the solid samples, which makes it suitable for industrial applications where bulk materials are treated. The amount of electromagnetic energy, which is transferred into the biomaterial between the electrodes in the form of heat, relies on dielectric properties of the biomaterials, the clearance between electrodes, the RF-supplied voltage and frequency. Despite low frequency, if biomaterials are soaked by an appropriate ionic solution in order to reach a suitable dielectric loss factor and small clearance between electrodes, together with a sufficiently high voltage applied to the biomaterials, within a short period of time, the temperature of the whole biomaterial can increase adequately to produce steam within cells. A preliminarily test which was conducted for rhizome particles of *Podophyllum peltatum* containing podophyllotoxin (Izadifar and Baik, 2008) indicated that a packed bed of particles soaked with ethanol could reach 70°C in four seconds. For some poorly or slowly germinating seeds, the application of RF can increase the seed-coat impermeability, but avoid damage on seed by a mechanical abrasive process (Nelson, 1985).

HYBRID PROCESSES

Toepfl and colleagues (2005) compared the effects of the various pretreatments, including PEF, mechanically pressurized, enzymatic, and freeze–thawing method, on the total permeabilisation of apple and potato tissues. PEF treatment required the lowest energy input in the range of 1–5 kJ/kg. In contrast, the energy consumption of 20–40 kJ/kg were associated with mechanical, 60–100 kJ/kg for enzymatic, approximately 250 kJ/kg for thermal, and approximately 280 kJ/kg for the freezing–thawing method, respectively. From the view point of energy saving, PEF may be a good choice for the pretreatment of solid materials for the extraction. However, non-uniform distribution field strength of PEF may reduce the popularity of the technique.

There seems to be no perfect method that can satisfy all the requirements as yet. Thus, hybrid applications of each method might be alternative solutions. For example, hardwood or agricultural stems can be processed by steam explosion to break down supporting frameworks in the cell walls. Then chemical pretreatment, particularly the alkaline method, can be applied to destroy the structure of the lignin in cells, or at least make them more accessible for further hydrolysis. There have been more and more reports on emerging hybrid processes to achieve both effectiveness and efficiency. Combinations of ultrasonication and enzymatic hydrolysis (Bermejo et al., 2004) promote cell-disruption efficiency significantly. Sun and Chen (2008) reported the improvement of the enzymatic hydrolysis of lignocellulosic biomass by aqueous glycerol pretreatment. The enzymatic hydrolysis yield obtained was up to 90% in 48 hours for the pretreated fiber of wheat straw. The fibrolytic enzyme activity of carboxymethyl cellulase (CMCase) and avicelase activity on the rice straw was tested (Chen et al., 2008). The activities of both CMCase and avicelase are promoted by adding sodium hydroxide (SH), which means the enzymes favor more in alkaline environment in their study. With alkaline/oxidative (A/O) pretreatment and the enzymatic hydrolysis of aquatic plants, sugar production achieved was three times more than that of untreated samples (Mishima et al., 2006). The application of ultrasound, MW, or steam explosion, can also facilitate the enzymatic hydrolysis of lignocellulosic biomass to get a higher yield in a shorter time period (Alvira et al., 2010). In food freezing–thawing cycles, the application of high pressure in freezing can provide uniform and rapid ice nucleation through

the whole sample, while MW and ultrasound can also offer a quick thawing process to improve the overall product quality of vegetables and fruits (Li and Sun, 2002).

SUMMARY AND CONCLUDING REMARKS

Active researches have been conducted to study the effects of different pretreatments on cell disruption. Each method reviewed in this paper has its own technical advantages and disadvantages.

From the viewpoint of industrial application, the energy consumption, processing time, process mode (batch or continuous), and cost of operation are very important to make the technology commercially feasible. With the exception of the freeze–thawing process, physical treatments such as HP, PEF, and ultrasonication seem to be valuable technologies to fulfill the current demand for saving energy.

Furthermore, methods including HP, PEF, ultrasound, and freeze–thaw can be operated at lower temperatures. The processing time for these methods in the magnitude of second to minutes is also very competitive in comparison with process duration in hours for enzymatic or chemical treatment. These physical pretreatment methods appear to be effective alternatives because they will not produce any harmful residues by adding additional materials into the system, which may bring pollution issues. During HP, PEF, freeze–thaw pretreatments, most bioactive compounds remain intact and there is minimal degradation of color or flavor, which shows promising potential for better food-quality processing techniques.

Nevertheless, physical methods have their own intrinsic disadvantages that have prevented their popularity. The disadvantages include high initial capital costs for high-pressure applicators in HP application, limited choice of solvent type in PEF application, high energy consumption in freeze–thawing applications, or non-uniform energy distribution in ultrasonication. The effectiveness of these techniques also depends on the characteristic of raw materials. Most of reports about HP or PEF pretreatment are focused on the physical changes of soft tissues of vegetables, fruits, or meat. There is little publication concerning HP, PEF, or freeze–thaw treatments of rigid plant tissues. Although chemical methods may draw attention to environmental issues, their high effectiveness on cell wall disruption on plant fibers still makes them available as a valuable pretreatment. For highly lignified tissues, the enzymatic or chemical pretreatments are more suitable methods for application. A good understanding of each technique is essential to select proper methods according to specific purposes for extraction in the food or bioprocess.

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