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Microwave assisted extraction of bioactive compounds: A brief review

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Microwave assisted extraction has been a topic of research for last decade and has gained quite momentum in the recent years. This article summarizes the different conventional methods of extraction of bioactive compounds and their drawbacks and it is felt that microwave assisted extraction is found to be a better alternative. Several new and novel extraction techniques like microwave assisted extraction (MAE), ultrasound assisted extraction (UAE), supercritical fluid extraction (SFE) are also briefly described. Mechanisms of MAE, types of instruments used and factors affecting MAE have been described briefly in this review article. Finally, recent research works with their inferences in the field of microwave assisted extraction (MAE) for bioactive compounds are drawn and presented in this manuscript.

Keywords: Bioactive compounds, conventional extraction, advanced extraction techniques, microwave assisted extraction (MAE), insights of MAE, recent studies in MEA.

Introduction

Extraction is a separation process in which the desired compound is separated from its matrix. It can either be a liquid-liquid extraction or a solid phase extraction. The extraction process is carried by means of a liquid immiscible solvent. The extent and rate of extraction is governed by solubility of desired compound in the solvent. Following properties of solvent are desired: (1) miscible with the desired compound, (2) immiscible with other components, (3) the boiling point of the solvent should well below the melting point of the solute in case of solid and boiling point in case of liquid, (4) favorable temperature coefficient, (5) thermal and chemical stability, (6) non-toxic, (7) cheap and (8) corrosion resistant.

Focused compounds:

Extraction process is widely used for obtaining bioactive compounds from plants, nutraceuticals, phytochemicals, and medicinal compounds[1]. Several reports have shown application of microwaves for extraction of residues of insecticides and pesticides and herbicides from sample.

Importance of extracted compounds:

Bioactive compounds comprise of essential oils, flavors and antioxidants which have varied and wide applications in food processing industries to enhance the nutritional and health properties of food products and also to increase their shelf life. Phytoconstituents include biologically significant compounds found in plants but not necessarily nutrients. They are responsible for color, smell, taste and other properties. They can be categorized into phenolics, alkaloids, saponins, glycosides, terpenes, steroids, tannins, anthraquinones. Nutraceuticals are any substances that are food or part of food but along with it they also provide medical benefits including prevention or cure of a disease.

Recovery of compounds:

Conventional methods of extraction include percolation, decoction, maceration, digestion, infusion and Soxhlet extraction. Although these techniques being widely used, they resulted in low yield of compounds with huge solvent requirement and large extraction times. This led to development of advanced techniques which along with providing better yields required less solvent and extraction time.

Conventional extraction methods

Following are the conventional methods of extraction[2]:

In ***Infusion***, the most used solvent being boiled water, is poured over the matrix and allowed to stand for around 15 min with periodic stirring and then liquid is filtered off. In the method of ***Decoction***, desired compound containing matrix is boiled along with specified volume of water for a fixed time. It is allowed to cool down before filtration. In ***Maceration***, the matrix is soaked in the solvent inside a corked container for a period of 3–7 days with proper agitation until the entire soluble material gets dissolved. Then the liquid is strained and residue is pressed to obtain more liquid. Both the liquids are combined and filtered. ***Digestion*** is just the modification of maceration in which the solvent is warmed to facilitate faster and better dissolution of required compound into the solvent. Hence, it can be used for extraction of thermolabile constituents. In ***Percolation***, powdered matrix is soaked with suitable solvent for about 24 h in a percolator. Then more solvent is added allowed to stand for fixed time. Process is repeated to get maximum yield. ***Soxhlet Extraction***[3] is used where desired component is slightly soluble in the solvent. In this method, powdered matrix is wrapped in a thimble usually made up of filter paper and placed in the holder. This is fitted over distillation flask and a condenser is fixed over the thimble holder. Solvent in distillation flask is vaporized and reaches the condenser. It is then passed through the powdered matrix. This process is repeated until all the material is extracted

There are various limitations associated with the conventional methods of extraction such as: (i) large solvent requirement, (ii) large extraction time, (iii) unsuitability for extraction of thermolabile substances, (iv) unsuitable for compound in large quantity in the matrix and (v) low yield and extraction efficiency.

Advanced extraction techniques

To overcome these shortcomings and to get the desired yield without the use of huge amount of solvent or large extraction time various advanced methods have been developed.

In **microwave assisted extraction**[4], heating of matrix is done by the means of microwaves. Microwaves possess electric field and magnetic fields which are mutually perpendicular. In this way the solvent and matrix are heated subsequently in a very short span of time. **Ultrasound assisted extraction**[5] involves the use of ultrasound waves for carrying out the extraction process. UAE follows the principle of acoustic cavitation thereby breaking the cell walls and increasing the rate of release of desired compounds. It can be used for extraction of thermolabile compounds since it does not require very high temperatures in the **supercritical fluid extraction**[6], diffusivity and solubility are increased manifolds in supercritical fluid as compared to liquid or gas. The process is continued for a fixed time which is pre-determined and is suitable for complete extraction. Solvent can be separated from the required constituent easily by reducing the temperature and pressure of the solvent. but it is an expensive and elevated pressures restrict the choices of vessels. **Accelerated solvent extraction**[7] is an advanced technique to extract desirable constituent from solid or semi-solid matrix using a liquid solvent at elevated temperature and pressure conditions. Extraction process becomes more efficient since solubility of solute in solvent is enhanced. Thermolabile substances cannot be extracted.

Microwave assisted extraction (MAE)

In microwave assisted extraction, heating of matrix is done by the means of microwaves. Microwaves possess electric field and magnetic fields which are mutually perpendicular. Heating is brought about by electric field by means of ionic conduction and dipole rotation. Components absorb microwave energy depending upon their dielectric properties.

Properties of microwaves[8]*:*

(1) Microwaves lie between infrared waves and radio waves in electromagnetic spectrum.

(2) These have wavelengths between 0.01 m to 1 m.

(3) These can be operated in a frequency range between 300 MHz to 300 GHz.

(4) Energy in a microwave photon is 0.037 kcal/mol which is relatively low compared to that required to break a bond hence the changes brought about by microwave heating are purely kinetic.

(5) Microwaves transfer energy in seconds way faster than the time required by a molecule to relax.

Mechanism of MAE

Heating of solid matrix is brought about by dual mechanisms of dipolar rotation and ionic conduction. Heating may be due to either one of them or both the mechanisms taking place simultaneously. In **ionic conduction**, ions try to migrate in accordance with changing electric field. In doing so they suffer collisions with each other and solvent molecules. Furthermore, if solvent molecules resist the motion of ions, friction is generated eventually leading to liberation of heat. In **dipolar rotation**, polar molecules try to align themselves in phase with the changing electromagnetic field. However due to inertia and inter-molecular forces of attraction, some resistance is offered which leads to generation of heat.

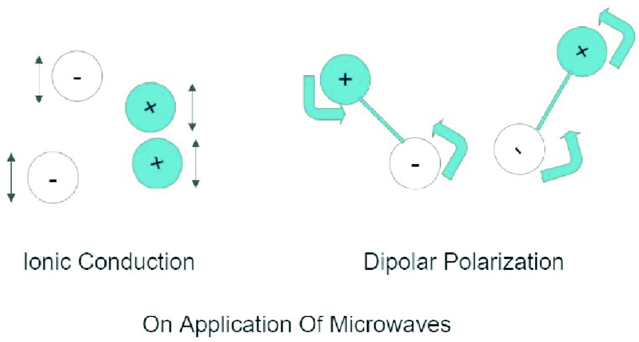

Fig. 1. Mechanism of MAE.

MAE system[9]

Microwave assisted extraction can be carried out in two types of vessels:

Focused MAE system (open vessel):

In focused vessel system, microwaves are irradiated at a particular position in the vessel where the sample is placed. The pressure is atmospheric since it is an open vessel. A condenser is fixed on the top of the extraction vessel to prevent the loss of volatile materials. It is used for the extraction of thermolabile substances since temperature cannot be increased beyond the boiling point of solvent. Excess solvent can be removed. However, slightly greater time is required for extraction.

Closed vessel MAE system:

In closed vessel, extraction is carries out at elevated temperature and pressure conditions. High temperature ensures higher solubility, diffusion and rate of mass transfer of solute from matrix into the solvent and elevated temperature ensure that physical state of solvent is liquid when temperature is increased beyond the boiling point of solvent. The system must be cooled before opening the vessel to prevent any loss of volatile substances to atmosphere. Materials of construction of vessel are chosen such that it can withstand elevated pressures. Since the vessel is closed, hazardous fumes, if any, are not released in the environment.

Solvents used

Dielectric constant, ε' represents the ability of the compound to be polarized by a changing electric field. Dielectric loss factor, ε'' is defined as the capacity of a molecule to convert the absorbed microwave energy into heat and dissipate it to the surroundings. Dissipation factor is expressed as:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Higher the dissipation factor higher will be the electromagnetic energy converted to heat energy. So, solvent should be such that it has high dielectric constant and high dissipation factor. Usually polar solvents like ethanol, methanol and water are used. Out of these, water has low dissipation loss factor and methanol is toxic, so most commonly used polar solvent is ethanol.. Most commonly used combination is that of ethanol-hexane.

Factors affecting MAE[10]

Solvent:

Solvent should be such that solute is highly soluble in it. It should also have high dielectric constant to absorb microwave energy and high dissipation factor so that absorbed microwave energy can be easily converted into heat energy and dissipated to solid matrix.

Solvent to feed ratio:

Although higher solvent means easy recovery of solute, however, large amount of solvent implies that greater microwave power will be required to heat it up eventually leading to higher temperatures and high extracting time. Excess solvent may also cause undesirable dissolution of other constituents. Values of solvent/feed range from 10:1 to 50:1 (v/v).

Temperature:

High temperature enhances the solubility of solute in the solvent. However, very high temperature may lead to degradation of the solute especially if it is a thermolabile substance. Also, high temperature increases the microwave power and extraction time leading to an increase in overall cost.

Extraction time:

Extraction time refers to overall time taken by the process right from heating till recovery. The amount of analyte extracted increases with increase in extraction time but may also cause deterioration of the solute due to longer exposure to heat.

Microwave power:

Microwave power should be chosen such that extraction time is minimized without the degradation of solute. For closed systems it varies from 600 W to 1000 W and for open systems it is around 250 W.

Matrix characteristics:

Size of matrix particles is also important. Fine particles imply larger surface area and hence better contact between solvent and matrix.

Latest MAE techniques

Nitrogen-protected MAE:

To prevent the oxidation of active constituents which may be present in the matrix, nitrogen gas is used at high pressure. First air is removed and vacuum is created then pressurized nitrogen is filled with the help of a gas cylinder. This type of extraction is always carried in a closed vessel system. It is mainly used for extraction of ascorbic acid from various types of peppers and guava.

Vacuum MAE:

This method is useful for thermolabile substances as the temperature is kept low enough to prevent the deterioration of solute. In absence of air and thus oxygen, activation or oxidation or oxygen sensitive constituents is also avoided. Moreover, amount of solvent required is also less as it continues to boil and be refluxed for proper dissolution of solute.

Solvent free MAE:

In this method, the water that is naturally present in the plant matter is used for absorbing microwave heat and no other external solvent is needed. It is majorly used for extraction of essential oils from plant materials. *In situ* water absorbs microwave energy and get vaporized. This produces tremendous pressure on the cell walls and leads to its rupturing. Essential oil easily comes out and evaporates. A condenser is installed to recover essential oil.

Ultrasound based MAE:

In this process an ultrasound transducer and open microwave is used simultaneously. This combination reduces the microwave power and extraction time by enhancing the rate of mass transfer. Amount of solvent required is also less.

Recent studies on MAE:

Microwave Assisted Extraction has been widely used for various laboratory experiments and theoretical concepts by researches. Some of the recent works have been tabulated in Table 1 along with the major findings of the MAE techniques that includes source of extraction, component being extracted, solvent, optimum conditions and the yield of the experiment carried out.

Table 1. Recent studies on MAE process to extract bioactive compounds

Authors	Compound	Source	Solvent	Conditions	Yield/inference
Kurtulbas *et al.*, 2020 (11)	Anthocyanin	*Hibiscus sabdariffa*	35 ml DES in 50% Water (v/v)	1. 550 W microwave power 2. 180s MAE time	2.961 mg C3G/g-DH
Belwal *et al.*, 2020 (12)	Berberine	Berberis	Methanol	1. S:L ratio 1:70 (g/ml) 2. Microwave power 598 W	46.38 mg/g
Deng *et al.*, 2019 (13)	Saponins	*Sapindus mukorossi*	40% Ethanol	1. Extraction time of 13 min 2. L:S ratio of 19 mL/g 3. Microwave power of 425 W	Extraction rate of 280.55±6.81 mg/g
Yamani *et al.*, 2019 (14)	Gallic acid	*Acacia arabica* bark	20% Methanol	1. Solid/liquid ratio 1:40 (g/mL) 2. Irradiation power 20% 3. 2 extraction cycles, 5 min each	10.59 (mg/g) gallic acid
Chenn *et al.*, 2019 (15)	Pectin	Hawthorn wine pomace	Sodium hexametap hosphate	1. S:L ratio of 1:9 2. Microwave power 440 W 3. Microwave time of 80 s	72.89±0.45%

Table-1 (contd.)

Zhangxing *et al.*, 2019 (16)	Tea polyphenols	Tea leaves	Magnetic ionic liquid (C3MIMFeCl4)	1. 200 W 2. Solid:liquid ratio is 1:20 3. Extraction time 7 min	1. Efficiency of 0.8 mol/L 2. Faster than UAE
Dieza *et al.*, 2019 (17)	Anthocyanin	Wine Lees	40% Ethanol	1. 300 W microwave power 2. 90 s MAE time	6.2 mg MLVE/g DL
Sari *et al.*, 2018 (18)	Pectin	*Watermelon rinds*	Acetic acid	1. Microwave power 279.3 W 2. 12 min irradiation time	25.79%
Sladkova *et al.*, 2018 (19)	Polyphenols	Spruce bark	96.6% Ethanol	1. L/S ratio is 12.0 mL/g 2. Extraction temp. of 100°C 3. Extraction time of 13.4 min	7.61%
Caleja *et al.*, 2017 (20)	Rosmarinic acid	*Melissa officinalis* L.	25.5±0.9% of ethanol	1. 26.5±2.1 min 2. 108.6±10.2°C temp. 3. 400 W power level	49.4±2.3 mg RA/g plant dw
Krishnan and Rajan, 2017 (21)	Flavonoids	*Phyllanthus emblica*	Water	1. Solvent: Feed 40 mL/g 2. Temperature 100°C	1.0402%
Pinela *et al.*, 2016 (22)	*p*-Coumaric acid derivative	Tomato	Water	1. Time 3.15 min 2. Temperature 144.64°C 3. S/L 45 g/L	24.8±0.9 mg/g extract
Simic *et al.*, 2016 (23)	Polyphenolics	Chokeberries (*Aronia melanocarpa*)	53.6% Ethanol	1. Microwave power of 300 W 2. Extraction time of 5 min	420.1 mg (GAE)/ 100 g of fresh plant material
Mustapaa *et al.*, 2015 (24)	Polyphenols	*Clinacanthus nutans* Lindau	50% Ethanol	1. 300 W microwave power 2. 30 s extraction time	8.08 mg/GAE/g DS
Krishnan and Rajan, 2016 (25)	Flavonoids	*Terminalia bellerica*	Water	1. Solvent:Feed (5:40 mL/g) 2. Temperature (40–100°C)	25.21 mg/g

Conclusion and future scope

MAE has been used rapidly and successively in the recent years. Its major benefits are reduced extraction time, less solvent requirement and higher yield. However, there is a scope of development for the post extraction processes like recovery, clean up etc.

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