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THE DEVELOPMENT OF MICROWAVE ASSISTED EXTRACTION TECHNIQUES

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ABSTRACT

Microwave-assisted extraction (MAE) or simply microwave extraction is a relatively new extraction technique that combines microwave and traditional solvent extraction. Application of microwaves for heating the solvents and plant tissues in extraction process, which increases the kinetic of extraction, is called microwave-assisted extraction. The use of MAE in natural products extraction started in the late 1980, though the technological developments, it has now become one of the popular and cost-effective extraction methods available today, and several advanced MAE instrumentations and methodologies have become available, e.g., pressurized microwave-assisted extraction (PMAE) and solvent-free microwave-assisted extraction (SFMAE). This chapter provides an overview of the MAE and presents a number of specific proto collateral products extraction.

KEYWORDS: Microwave Assisted Extraction, Close/Open MAE System, Development of MAE, Factor Affecting of MAE, Guidelines for MAE.

NTRODUCTION

Microwave-assisted extraction (MAE) is a relatively new extraction technique that combines microwave and traditional solvent extraction. Solvent extraction has been intensively used for isolation of important compounds and for the qualitative and quantitative analysis in various fields such as environmental analysis, food agricultural analysis, pharmacological drugs and herbal medicine. In MAE, the extraction occurs as a result of changes in the cell structure caused by electromagnetic waves. It has been proposed that the extraction acceleration observed in MAE may be due to the heat and mass transfer gradients working in the same direction. Using microwaves for heating the solvents and plant tissues increases the kinetics of extraction, and various advantages are thus obtained over traditional solvent extraction, including shorter extraction times, higher extraction rates, lower costs, and less solvent use. MAE has been employed in the extraction of various compounds from natural sources, in leaves, terpene from must, and gossypol from cottonseeds. The potential natural anticancer drugs like vincristine, vinblastine and Taxol can be the best example. Recent years have shown a growing popularity and faith in the use of herbal medicine worldwide. This may be because of the realization that modern synthetic drugs have failed to provide a "cure all" guarantee to most of the human diseases with often producing undesirable side effects, which at the end turnout to be more problematic than the actual disease itself. The herbal medicine provides a ray of hope through its cocktail of phyto-compounds, which are believed to act in a synergistic manner, providing excellent healing touch with practically no undesirable side effects, provided its quality is assured off.

Principle

Even though dried plant material is used for extraction in most cases, but still plant cells contain minute microscopic traces of moisture that serves as the target for microwave heating. The moisture when heated up inside the plant cell due to microwave effect, evaporates and generates tremendous pressure on the cell wall due to swelling of the plant cell. The pressure pushes the cell wall from inside, stretching and ultimately rupturing it, which facilitates leaching out of the active constituents from the ruptures cells to the surrounding solvent thus improving the yield of phyto-constituents. This phenomenon can even be more intensified if the plant matrix is impregnated with solvents with higher heating efficiency under microwave. Higher temperature attained by microwave radiation can hydrolyse ether linkages of cellulose, which is the main constituent of plant cell wall, and can convert into soluble fractions within 1 to 2 min. The higher temperature attained by the cell wall, during MAE, enhances the dehydration of cellulose and reduces its mechanical strength and this in turn helps solvent to access easily to compounds inside the cell. In order to study cell damage during the MAE experiments, tobacco leaf samples were examined by scanning electron microscopy. Scanning electron micrographs of the untreated sample, heat-reflux extraction sample and MAE sample revealed that there were no structural difference between heat-reflux extraction and those of untreated samples, except few slight ruptures on the surface of the sample. However, the surface of the sample was found greatly destroyed after

MAE. This observation suggests that microwave treatment affects the structure of the cell due to the sudden temperature rise and internal pressure increase. During the rupture process, a rapid exudation of the chemical substance within the cell into the surrounding solvents takes place.

Mechanism

The fundamentals of the microwave extraction (MAE) process are different from those of conventional methods (solid–liquid or simply extraction) because the extraction occurs as the result of changes in the cell structure caused by electromagnetic waves. In MAE, the process acceleration and high extraction yield may be the result of a synergistic combination of two transport phenomena: heat and mass gradients working in the same direction. On the other hand, in conventional extractions the mass transfer occurs from inside to the outside, although the heat transfer occurs from the outside to the inside of the substrate. In addition, although in conventional extraction the heat is transferred from the heating medium to the interior of the sample, in MAE the heat is dissipated volumetrically inside the irradiated medium.

During the extraction process, the rate of recovery of the extract is not a linear function of time: the concentration of solute inside the solid varies, leading to a non-stationary or unsteady condition. A series of phenomenological steps must occur during the period of interaction between the solid-containing particle and the solvent effectuating the separation, including.

(1) Penetration of the solvent into the solid matrix.

(2) Solubilisation and breakdown of components.

(3) Transport of the solute out of the solid matrix.

(4) Migration of the extracted solute from the external surface of the solid into the bulk solution.

(5) Movement of the extract with respect to the solid.

(6) Separation and discharge of the extract and solid.

The development of MAE techniques

In general, MAE systems are classified into multi-mode system and focused-mode system (mono-mode). Multi-mode system allows random dispersion of microwave radiation in cavity by a mode stirrer while focused system (mono-mode) allows focused microwave radiation on a restricted zone in cavity. Usually, the multi-mode system is associated with high pressure while the mono-mode system is employed under atmospheric operating pressure. However, mono-mode system can also run at high pressure. To avoid confusion in the classification of MAE, ‘closed system’ and ‘open system’ are used to refer to the system that operates above atmospheric pressure and under atmospheric pressure, respectively. For further understanding of the closed system and open system, schematic diagrams are illustrated in Fig. In a closed MAE system, the extractions are carried out in a sealed-vessel with different mode of microwave radiations. Extraction is normally carried out under uniform microwave heating. High working pressure and temperature of the system allow fast and efficient extraction. The pressure inside the extraction vessel is controlled in such a way that it would not exceed the working pressure of the vessel while the temperature can be regulated above the normal boiling point of the extraction solvent. Recent advancements in the closed system have led to the development of high pressure microwave-assisted extraction (HPMAE). The increase temperature and pressure accelerates microwave-assisted extraction due to the ability of extraction solvent to absorb microwave energy. Despite the fact that the closed system offers fast and efficient extraction with less solvent consumption, it is susceptible to losses of volatile compounds with limited sample throughput. Open system is developed to counter the shortcomings of closed system such as the safety issues and it is considered more suitable for extracting thermo-labile compounds. This system has higher sample throughput and more solvent can be added to the sys- tem at any time during the process. Basically, open system operates at more mild conditions. Its advantages and disadvantages are highlighted by luque-Garcia and luque de Castro. Open MAE system is widely used in the extraction of active compounds and is also used in analytical chemistry. This system operates at atmospheric conditions and only part of the vessel is directly exposed to the propagation of microwave radiation (mono-mode). The upper part of the vessel is connected to a reflux unit to condense any vaporized solvent. Besides that, multi-mode radiation can also be employed in open MAE system with the reflux unit.

Microwave Theory

Microwaves are non-ionizing electromagnetic waves of frequency between 300 MHz to 300 GHz and positioned between the X- ray and infrared rays in the electromagnetic spectrum. In modern day science microwaves serves two major purpose communication and as energy vectors. The latter application is the direct action of waves on materials that has the ability to convert a part of the absorbed electromagnetic energy to heat energy. Microwaves are made up of two oscillating perpendicular field’s i.e. electric field and magnetic field and the former is responsible for heating. Unlike conventional heating which depends on conduction – convection phenomenon with eventually much of the heat energy being lost to the environment. Whereas in case of MAE, heating occurs in a targeted and selective manner with practically no heat being lost to the environment as the heating occurs in a closed system. This unique heating mechanism can significantly reduce the extraction time (usually less than 30 min) as compared to Soxhlet. The principle of heating using microwave is based upon its direct impact with polar materials/solvents and is governed by two phenomenon's: ionic conduction and dipole rotation, which in most cases occurs simultaneously. Ionic conduction refers to the electrophoretic migration of ions under the influence of the changing electric field. The resistance offered by the solution to the migration of ions generates friction, which eventually heats up the solution. Dipole rotation means realignment of the dipoles of the molecule with the rapidly changing electric field.

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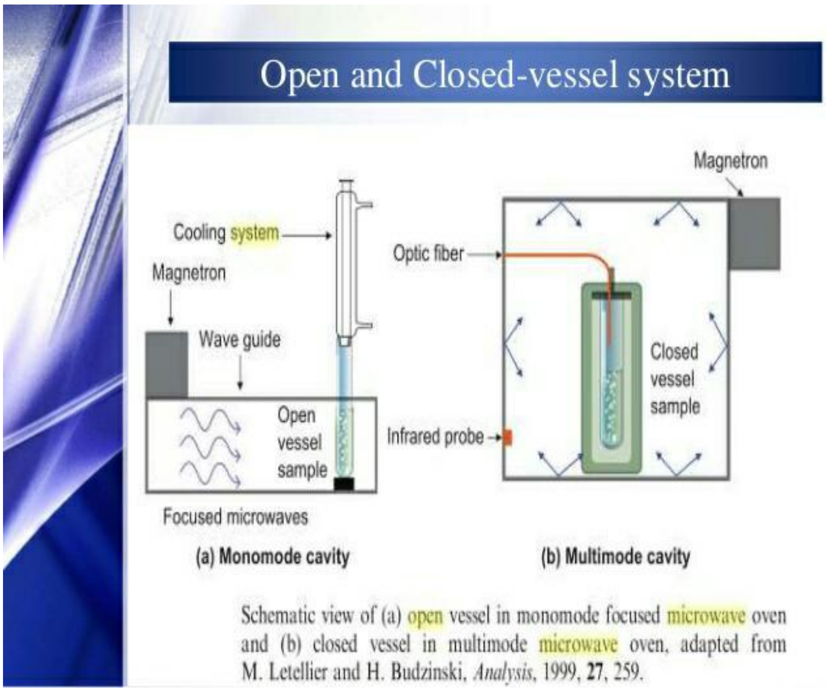
- **Close MAE system**



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- **Open MAE System**

Open system is developed to counter the shortcomings of closed system such as the safety issues and it is considered more suitable for extracting thermo-labile compounds. This system has higher sample throughput and more solvent can be added to the system at any time during the process. Basically, open system operates at more mild conditions. Open MAE system is widely used in the extraction of active compounds and is also used in analytical chemistry. This system operates at atmospheric conditions and only part of the vessel is directly exposed to the propagation of microwave radiation (mono-mode). The upper part of the vessel is connected to a reflux unit to condense any vaporized solvent. Besides that, multi-mode radiation can also be employed in open MAE system with the reflux unit.

Factors affecting the capacity of MAE

The efficiency of MAE depend on the selection of the operating conditions and the factors affecting the extraction mechanism. The factors that may affect the yield of extraction are solvent nature, extraction time, microwave power, temperature, sample characteristic, effect of stirring, etc. It is important understand the effects and interactions of these factors on the MAE processes.

1. Solvent Nature

The selection of suitable solvent in MAE extraction process depends on the solubility of the target analyse, solvent's penetration and interaction with sample matrix and its dielectric constant. Aqueous solution of certain organic solvent is desired for some extractions as the presence of water would improve the penetration of solvent into sample matrix and thus enhance heating efficiency. Other organic solvents such as ethanol, methanol, and acetone are also found to be effective in extraction. For instance, methanol was used to extract phenolic compounds from grape skins and seeds and higher yield of polyphenols was obtained as compared to extraction using ethanol but the latter extract had stronger antioxidant properties. Solvent toxicity is also evaluated in selecting suitable solvent for MAE. It is important to note that the selection of a solvent for MAE can not be deduced from the conventional extraction methods as solvents that work well in conventional techniques might not be a good solvent for MAE. For example, diethyl ether that has been used extensively in solubilizing steroids from fragrance family is not suitable as MAE solvent. However, a modifier can be added to the solvent to enhance its overall performance. Water was added as modifier to diethyl ether to enhance microwave heating efficiency in the extraction of steroids from Rodgersia aesculifolia Batal. In addition, ethanol or water can be added into poor microwave absorber such as hexane to improve the extraction efficiency as in the case of ginger extraction by MAE. Moreover, acetone can be enhanced by adding portion of methanol in MAE of curcumin.

2. Microwave Power

High microwave power might cause poor extraction yield due to the degradation of thermal sensible compounds. In general, the extraction yield increases proportionally with increasing microwave power up to a limit before the increase becomes insignificant or decline. Microwave power provides localized heating in the sample and it acts as a driving force for MAE to destroy the plant matrix so that analyse can diffuse out and dissolve in the solvent. Increasing the power will generally improve the extraction yield and result in shorter extraction time.

3. Extraction Time and Cycle

Apart from interactive effect on temperature, the influence of the microwave power can be extended to the extraction time. Over exposure to microwave radiation even at low temperature or low operating power was found to decrease the extraction yield due to the loss of chemical structure of the active compounds .In order to avoid the risk of thermal degradation and oxidation, the extraction time of MAE usually varies from few minutes up to half an hour with the exception of solvent-free microwave-assisted extraction (SFME) where longer extraction time of 1 h is necessary for complete extraction of essential oil.

4. Plant Matrix Characteristic

The characteristics of the sample also effects on the performance of MAE. The extraction sample is usually dried, powdered and sieved into fine powder prior to the extraction for optimum extraction yield. Moreover, fine sample treated by solvent for 90 min prior to extraction can enhance the heating efficiency of MAE, promote diffusion and improve mass transfer of active compounds to the solvent.

5. Temperature

Microwave power and temperature are very interrelated to each other and needs to be given special attention particularly when working with closed vessel system. In closed vessel systems, temperature may reach well above the boiling point of the solvent. This elevated temperature does indeed result in improved extraction efficiencies since desorption of analyse from active sites in the matrix will increase. Additionally solvents have higher capacity to solubilize analyse at higher temperature while surface tension and solvent viscosity decreases with temperature, which will improve sample wetting and matrix penetration respectively. Increase in temperature is also associated with increase in pressure in closed systems, which can raise safety concerns. Temperature was found to be a significant factor in the extraction of paclitaxel. Temperature can be effectively controlled in open vessel system by proper combinations of extracting solvents which heat up differently. Thorough study of different

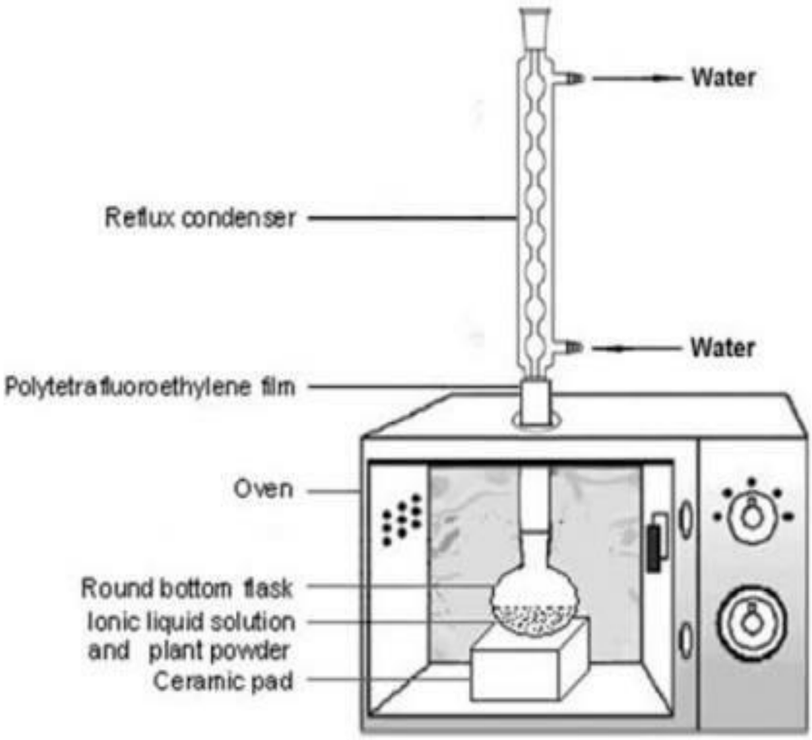
MAE investigations and from the personal experience of the authors, we present a brief schematic MAE for open vessel extraction systems, performed under atmospheric pressure.

General MAE procedures

The extraction of active ingredients from plants involves several steps starting from the initial sample preparation followed by the extraction of active ingredients to the clean up procedure and quantification analysis.

1. Sample Preparation

As illustrated in Fig. 4, sample preparation involves that the desired parts of the plants are oven dried or sun dried to remove the moisture. The drying temperature is kept between 40 - 60 ◦C to avoid thermal degradation. The dried sample is then pulverized and sieved to sizes of 40–60 mesh number to promote efficient extraction when expose to solvent. In certain cases, sample pre-treatment prior to extraction is conducted to enhance the extraction process. This is done by soaking the samples in an extraction solvent such as water and methanol. As previously briefed in the case of solvent-free microwave-assisted extraction (SFME), the moisture of the sample matrix resulted from water pre-treatment is responsible for the extraction of the active ingredients.



In other cases, some undesired components of the samples were removed by pre-treatment with an organic solvent i.e. petroleum ether. This can be done by soaking the sample overnight to remove the lipids portion and chlorophyll.

2. Extraction Process

After sample preparation and pre-treatment, the sample is subjected to extraction. For modified MAE techniques, additional instruments are required. In the case of open microwave system, reflux unit is initiated and the condensing tube is connected to the extraction vessel inside the microwave cavity. As for UMAE, ultrasonic transducer is needed and is normally set to a power of 50W and frequency of 40 kHz. In the case of VMAE, the condensing tube is kept under vacuum to 40 KPa. In NPMAE, inert gas can be pressurized through the condensing tube in which the vessel is vacuumed. After proper setup, the sample is then irradiated under specific operating conditions. As in HPMAE of ginseng, the pressure of the vessel is allowed to reach up to 400 Kp.

Guidelines for selecting MAE techniques

The brief guidelines for selecting suitable techniques i.e. DMAE, NPMAE, CMAE, SFME, UMAE are listed in this section. The summary of the development of these extraction techniques are tabulated in Table 4 and the applications, advantages and drawbacks for each technique are also presented. Standard MAE is commonly employed either in open or closed systems to extract thermo stable compounds. For extraction of degradable active compounds, there are various modified MAE techniques that are suitable for the application. DMAE is suitable to extract degradable compounds that require multiple extraction cycles as the technique performs under mild conditions and in continuous manner. This technique promotes a fast and efficient analytical step, as it can be on-line coupled with HPLC analysis system. The drawbacks of this technique are that it has low throughput, inconvenient feeding and removal of sample and residue as well as requirement of additional equipment setup such as pumps and valves. Besides, for highly fragile compounds which pose high risks of oxidation and thermal degradation, VMAE is suitable as the extraction is carried out in vacuum condition and at low temperature. The extraction usually requires longer extraction time due to the mild condition. Alternatively extraction of thermal degradable compounds can also be achieved through NPMAE. It gives faster extraction than VMAE but requires additional extraction step. On the other hand, SFME is more preferable to be used in essential oil extraction and it is more efficient than the traditional HD method. In some circumstances in which the associated active compounds have low diffusion and difficult to be extracted, UMAE can be employed as it improves the mass transfer mechanism and reduces the extraction time. This technique can provide high activation energy or the impact energy required for the extraction to proceed. However, for other extraction cases, additional ultrasonic wave might not give higher yields due to the fact that microwave radiation alone is sufficient to overcome the activation energy of the extraction.

CONCLUSION

This method is more effective and cheaper than conventional method. In this technique time required for complete extraction is less as compared to the conventional techniques. Solvent required for extraction is less than the other techniques. Amount of extracted phenolic compounds is increase MAE for open and closed vessel systems have been given separately. Several studies have been reported on the comparison of MAE with other conventional techniques. In most of the cases Soxhlet has been used as the control experiment. The main advantage of MAE reside in the performance of the heating source. MAE is now widely accepted in analytical laboratories. The method developed using MAE, and a traditional method of extraction such as magnetic stirring, it was confirmed that MAE is a much faster method.

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