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Ionic liquids as green solvents in herbal extraction

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Abstract
Extraction of phytoconstituents by the use of ionic liquids is very advantageous when compared to conventional extraction methods because of the excellent properties of ionic liquids combined with greater efficiency of microwaves. Ionic liquids are not composed of molecules, but made up of ions. They are also considered as designer solvents because of choice of cations and anions according to the isolation of phytoconstituent. They are green solvents and so ecofriendly in nature as they do not evaporate volatile organic compounds (VOC) which are very harmful.

Keywords: extraction, phytoconstituents, ionic liquids, ecofriendly, green extraction

1. Introduction
Ionic liquids are the solvents which are also known as "Green solvents" due to their excellent ecofriendly properties like negligible vapour pressure, high thermal stability as they remain liquid over a temperature range of 200 to 300^0 C, non-flammable, wide range of miscibility with water and other organic solvents with good chemical stabilities (Chauvin and Olivier, 1995) [18]. One of the key important advantages of ionic liquids is the presence of large organic positive ions with a high polarizability. Therefore, ionic liquids are very good media for absorbing microwaves, thus leading to a very high heating rate (Chemat and Cravatto, 2013) [5].

2. Methods of extraction of herbals
There are two basic ways of extraction that is conventional and recent methods. Conventional extraction techniques includes maceration, percolation, decoction, infusion, enfleurage, soxhlation. All these conventional extraction techniques are used for the purpose of isolation of target compounds but they do not give desirable potential results due to: longer extraction time, large quantity of solvents consumed, higher energy consumed, thermal degradation of active compounds, lesser purity. Although several active phytoconstituents and high activity profile drugs have been discovered from plants but the quality and safety related problems of herbal drugs have still been a challenge for researchers.
Conventional extraction techniques does not gives desirable potential results, which can be done by recent extraction techniques. So, there has been a need for the better and newer extraction techniques in the herbal industry so that the extraction time and the cost of solvent can be decreased. Recent extraction techniques gives better yield value, lesser solvents consumption, more pure compounds in lesser extraction time.
Microwave Assisted Extraction technique when compared with other recent extraction techniques gives better results as shown by the literature. In case of microwave assisted extraction technique there is a problem of bumping of solvents because of instant high temperature inside the microwave. To overcome this problem, ionic liquids can be used instead of other solvents and it gives the best results through high extraction yield, high efficiency, lesser time, recyclability of solvents.

3. Ionic liquids in herbal extraction
Ionic liquids are the source of green extraction or green chemistry. A general definition of green chemistry is the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances (Earle and Seddon, 2000) [10].
In relation to green extraction of natural products, this definition can be modified as follows: "*Green Extraction is based on the discovery and design of extraction processes which will reduce energy consumption, allows use of alternative solvents and renewable natural products, and ensure a safe and high quality extract/product*" (Chemat *et. al*., 2012) [2]

4. Microwave assisted extraction principle and mechanism
4.1 Principle
The basic principle of microwave extraction is the changes in cell structure caused by electromagnetic waves. The target of microwave extraction is the heating in dried plant material and the minute microscopic traces of moisture that occurs in plant cells. The heating up of this moisture inside the plant cell due to microwave effect results in evaporation and generates tremendous pressure on the cell wall. This pressure then ruptures the cell wall results in exudation of active constituents from the ruptured cells occurs hence increasing the yield of phytoconstituents (Veggi *et. al*., 2013; Yuan *et. al.*, 2011) [14, 19].

4.2 Mechanism
The mechanism of microwave heating is the dipole rotation and ionic conduction through reversals of dipoles and displacement of charged ions present in the solute and the solvent. Ionic conduction is the electrophoretic migration of ions when an electromagnetic field is applied, and the resistance of the solution to this flow of ions results in friction that heats the solution. Dipole rotation means

rearrangement of dipoles with the applied field (Mandal *et. al.*, 2007) [15].

5. Advantages of Microwave Assisted Extraction technique over conventional extraction techniques are:

1) Uniform heating occurs throughout the material. 2) Process speed is increased. 3) Desirable chemical and physical effects are produced. 4) Floor space requirements are decreased. 5) Better and more rapid process control is achieved. 6) In certain cases selective heating occurs which may significantly increase efficiency and decrease operating cost. 7) High efficiency of heating. 8) Reduction in unwanted side reaction (reaction Quenching). 9) Purity in final product. 10) Improve reproducibility. 11) Environmental heat loss is save. 12) Reduce wastage of heating reaction vessel. 13) Selective heating i.e. heating selectively one reaction component. 14) Super heating: conventional heating is done from outside, therefore the core of solvent may be as much as 5ºC cooler than the edge, while in microwave, the core is 5ºC hotter than the outside, because of surface cooling, therefore in microwave, we can raise the boiling point of solvent by as much as 5ºC, an effect is known as super heating. (Himanshu K. Solanki, 2010) [7].

6. Significance of IL-MAE in herbal analysis

IL-MAE technique is much better in comparison of conventional as well as among recent techniques of extraction due to the following reasons:

- **Ecofriendly, greener extraction**: IL-MAE do not evaporate volatile organic compounds (VOC), so considered as ecofriendly and green extraction technique.
- **Quantitative improvement:** there is improvement in the yield value of compounds when ionic liquid based microwave assisted extraction (IL-MAE) is used.
- **Qualitative improvement:** more pure compounds are obtained when compared with those extracted from conventional methods.
- **Thermal degradation of active constituents:** because of longer extraction time, degradation of active constituents also takes place (Khupse and Kumar, 2010) [12].
- **Lesser time:** high heating rates of electromagnetic microwaves leads to exudation of active constituents from the cells in a very efficient way in a very shorter time.
- **Lesser energy consumption:** when lesser time is used for the extraction purpose, lesser energy is consumed. Hence, more efficient.
- **Lesser solvent consumption:** only a small amount of solvents are consumed for the IL-MAE.
- **Recovery of solvents:** solvents which are used for IL-MAE can be recovered also can be used for further extraction purpose (Tatke and Jaiswal, 2011) [13].

7. Ionic liquid based microwave assisted extraction (ILs-MAE)

Energy transfer is the main characteristic of microwave heating. Traditionally, in heat transfer of the conventional process, the energy is transferred to the material by convection, conduction, and radiation phenomena through the external material surface in the presence of thermal gradients (Cecilia and Erland, 2000) [1]. In contrast, in MAE, the microwave energy is delivered directly to materials through molecular interactions with the electromagnetic field via conversions of electromagnetic energy into thermal energy (Chemat and Cravatto, 2013) [5].

Due to the better properties of ionic liquids like low vapour pressure, high thermal stability, nonflammability, tunable chemical structures and physical properties, wide range of miscibility with water and other organic solvents- they are considered as the solvents for microwave assisted extraction techniques (Chunxia *et al*., 2012) [4].

Examples of Ionic liquid based microwave assisted extraction:

- Pectin from lemon peels (Huang *et al*., 2012) [9]
- flavonoids from *Bauhinia championii* (Wei *et al*., 2012) [16]
- hyperin and isoquercitrin from *Apocynum venetum* (Xiao *et al*., 2012) [9]
- *trans*-resveratrol from *Rhizma Polygoni Cuspidati* (Fu-You *et al*., 2007) [6]
- Podophyllotoxin from three Chinese medicinal plants *Dysosma versipellis, Sinopodophyllum hexandrum* and *Diphylleia sinensis* (Ya *et al*., 2011) [19]
- tannins from *Galla chinensis* (Chunxia, 2012) [4]
- biphenyl cyclooctene lignans from *Schisandra chinensis* Baill (Chun-hui *et al*., 2011) [3]
- Phenolic alkaloids present in the medicinal plant *Nelumbo nucifera* Gaertn (Yanbin *et al*., 2008) [20]
- rutin from Chinese medicinal plants (Huan *et al*., 2010) [8]

8. Future scope

It is expected that through IL-MAE technique, the environment friendly, economic and efficient processes will be developed for the extraction and isolation of important phytoconstituents from plants of therapeutic importance. New protocols can be developed and these protocols will probably have better profile than the conventional extraction techniques and thus have immense potential to get patented or adopted at industrial scale to reach the benefit up to the consumer level.

9. Conclusion

To obtain chief constituents from the plant entities there are various techniques of extraction through which they can be isolated. There are continuous efforts in the scientific research to develop or modify recent techniques of extraction for (i) maximum yield (ii) intact interested constituents (iii) safer and (iv) economic models. In this regard, Ionic liquid based microwave assisted extraction (ILs-MAE) has received maximum attention from research and industrial application point of view in the recent past.

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