Trends in Analytical Chemistry 71 (2015) 100–109

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Ultrasound: A clean, green extraction technology

Brijesh K. Tiwari *

Food Biosciences, Teagasc Food Research Centre, Dublin, Ireland

ARTICLE INFO

Keywords:
Clean extraction
Environment-friendly extraction
Green solvent
Extraction kinetics
Extraction mechanism
Extraction yield
Solvent-free extraction
Ultrasonic energy
Ultrasound-assisted extraction

ABSTRACT

The objective of this review is to discuss the ultrasound-assisted extraction (UAE) of various compounds using clean, green solvents. We also outline fundamental mechanisms and factors associated with the design and the development of clean, green UAE systems. Growing consumer demands for greener alternatives and natural ingredients that do not involve toxic chemicals and the environmental and health risk associated with the use of chemical solvents have attracted the interest of industries to sustainable, non-toxic routes of extraction. UAE can benefit the chemical industry in multiple ways:

- enhancing extraction yield;
- enhancing aqueous extraction processes without using solvents;
- providing the opportunity to use alternative clean and/or green solvents by improving their extraction performance; and,
- enhancing extraction of heat-sensitive components under conditions that would otherwise have low or unacceptable yields.

Contents

1. Introduction

The principal objective of an extraction process is to maximize the target-compound yield with no or minimal impact on properties of the target compound whilst minimizing the extraction of undesirable compounds. Conventional solid-liquid extraction (SLE) techniques, including maceration, infusion and "Soxhlet" extraction, are time consuming and use large amounts of solvents [1]. Several chlorinated solvents (e.g., chloroform, carbon tetrachloride, tetrachloroethylene, and chlorobenzene) and non-chlorinated solvents (e.g., acetone, methanol, and acetonitrile) are used for extraction from various matrices, depending on the properties of the target compound. Safety risks, toxicity of certain solvents and presence of solvent residues in target compounds coupled with low extraction yield have stimulated interest in developing environment-friendly (green) extraction technologies, which can minimize or eliminate the use of organic solvents. Commercial interest in more sustainable, non-toxic routes of extraction has increased, driven by growing consumer demands for greener alternatives and natural ingredients that do not involve toxic chemicals, and the environmental and health risks associated with use of chemical solvents.

A major challenge in extracting molecules from a complex matrix in a sustainable way is that these molecules are usually embedded within the matrix. While there is undoubtedly a clear need to develop affordable, safe, effective, ecologically-innovative extraction techniques, it is important that such techniques not only enable clean label status, but also ensure enhanced yields with minimal impact on the quality of the end product. A number of novel alternatives to conventional techniques have been proposed for the

* Tel.: +353 18059785; Fax: +353 18059550.
E-mail address: brijesh.tiwari@teagasc.ie

http://dx.doi.org/10.1016/j.trac.2015.04.013
0165-9936/

extraction of target compounds from various matrices, including ultrasound-assisted extraction (UAE), sub-critical and supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE), or novel pre-treatments, including high-pressure processing and pulsed electric field. These novel techniques offer tremendous potential to reduce or to eliminate the use of toxic chemical solvents, while improving process efficiency, and enhancing extraction yields and quality of the extract. These techniques are also known as cold extraction techniques, as temperature during the extraction process is comparatively low and does not affect the stability of extracted compounds. Novel techniques can also be used as a pre-treatment or in combination with environment-friendly, safe organic solvents to enhance extraction efficiency by improving cell-membrane permeability, which is the parameter governing extraction efficiency.

Among novel extraction techniques, the application of ultrasonics for extraction increased in recent decades due to the several disadvantages associated with conventional and some other novel extraction techniques, such as high capital investment, high energy consumption, high rejection of CO_2 and consumption of toxic organic solvents and their residues in the extract. UAE is the method of using ultrasound as a pre-treatment step or during SLE itself. UAE offers environment-friendly, clean extraction with several advantages. Also, ultrasound is relatively easy to use, versatile, and flexible, and requires low investment compared to other novel extraction techniques (e.g., SFE, pressurized solvent extraction or ASE).

Use of ultrasound is a novel clean, green extraction technology for various molecules and biomaterials, including polysaccharides, essential oils, proteins, peptides, fine chemicals (dyes and pigments) and bioactive molecules of commercial importance. We extensively review specific applications of ultrasound in food, environmental, pharmaceutical and analytical chemistry with a focus on analytical purposes. This review paper presents the most outstanding results, outlining less toxic, GRAS (Generally Recognized As Safe) chemicals involved in using ultrasound energy. We also demonstrate the relevance of UAE as a key clean, environment-friendly extraction technology.

2. Principles of UAE

The history of scientific advances and the discovery of ultrasound are rooted in the study of sound, with Sir Isaac Newton first proposing his theory of sound waves in 1687 [2]. The fundamental difference between sound and ultrasound is the wave frequency. Generally, sound waves are divided into three categories that encompass different frequency ranges:

- *audible waves* lie within the range of sensitivity of the human ear (10 Hz–20 kHz);
- *infrasonic waves* have frequencies below the audible range (<16 Hz); and,
- *ultrasonic waves* having frequencies above the audible range (>20 kHz) and less than microwave frequencies (up to 10 MHz).

The ultrasonic region of the spectrum is important from application and commercial perspectives. Ultrasound can also be broadly classified as low-intensity sonication (<1 W/cm^2) and high-intensity sonication (10–1000 W/cm^2). The former is typically used as a non-destructive analytical technique for quality assurance and process control, especially of physico-chemical properties, such as composition, structure and physical state of matter, while high-intensity sonication is employed for extraction and processing applications.

Various physical and chemical phenomena including agitation, vibration, pressure, shock waves, shear forces, microjets, compression and rarefaction, acoustic streaming, cavitation and radical formation are responsible for ultrasonic effect. Physical and biochemical effects of ultrasound are associated with frequency [e.g., physical effects dominate at lower frequencies of 20–100 kHz, whereas chemical effects dominate at frequencies of 200–500 kHz, and, at higher frequencies (>1 MHz), acoustic streaming effects are more dominant.

The main driving force for the extraction effects of sonication is acoustic cavitation. When ultrasound propagates through any medium, it induces a series of compressions and rarefactions in the molecules of the medium. Such alternating pressure changes cause the formation and, ultimately, the collapse of bubbles in a liquid medium. This phenomenon of creation, expansion, and implosive collapse of microbubbles in ultrasound-irradiated liquids is known as "acoustic cavitation".

Cavitation bubbles formed are roughly divided into two types, namely transient cavitation (inertial) and stable cavitation (non-inertial). Stable cavities are relatively long-lived gas bubbles and exist for many cycles of compression and rarefaction [3]. Transient cavitation or inertial cavitation bubbles exist for a very short period, sometimes less than one cycle, and collapse violently [4,5]. There are many thousands of such bubbles in a liquid, some of which are relatively stable, but others expand further to an unstable size and undergo violent collapse to generate temperatures of about 5000 K and pressures of the order of 50 MPa [3,6–8] at a minuscule level. Theoretical calculations using hydrodynamic models of cavitational collapse have reported temperature and pressure estimates of 2000–10,000 K and 100–1000 MPa, respectively [9]. Temperature and pressure changes that occur from these implosions cause shear disruption, thinning of cell membranes and cell disruption, resulting in enhanced solvent penetration into cells and amplification of mass transfer of target compounds into the solvent. The implosion of cavitating bubbles also generates turbulence at a microscopic level, high-velocity inter-particle collisions and agitation in microporous particles of the matrix, which accelerates the diffusion [10–12]. Ultrasonic waves also facilitate hydration and swelling of the matrix with an enlargement of pores that increases the diffusion of solvent into the matrix and increases mass transfer. Hydration and swelling effects are advantageous when a dry matrix is used for UAE.

The ability of ultrasound to cause cavitation depends upon its characteristics (e.g., frequency and intensity), medium properties (e.g., viscosity and surface tension) and ambient conditions (e.g., temperature and pressure). The high-shear energy created by the cavitation effect is employed for applications including particle modification in liquids, release of cellular components and molecular structures, and de-aeration of liquids and surfaces. For extraction applications, formation and collapse of cavitation bubbles also depend on solvent properties. For example, vapor pressure governs intensity of collapse; surface tension and viscosity govern the transient threshold of cavitation. Chemical reactivity of the solvent dictates the primary and secondary sonochemical reactions.

The chemical effects of ultrasound have been studied extensively over the past century. Under the extreme temperature and pressure conditions, highly reactive radicals are generated. For example, if water is the medium, H$^\bullet$ and OH$^\bullet$ radicals are generated by the dissociation of water ($H_2O \rightarrow OH^- + H^+$). Both stable cavitation and an increase in the number of active bubbles can be expected to increase the amount of hydroxyl radicals generated as the ultrasound frequency increases. Ashokkumar and Sunartio [13] observed an increase in •OH radicals in water with the increase in ultrasonic frequencies from 20 kHz to 358 kHz followed by a decrease in •OH yield with an increase in frequency from 358 kHz to 1062 kHz. A plausible explanation can be the shortening of the acoustic cycle at high frequencies, thus restricting the amount of water vapor that can evaporate into the bubble during the expansion phase of the acoustic cycle. This decrease in the amount of water