Ultrasonics Sonochemistry 22 (2015) 149–154

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Changes of gallic acid mediated by ultrasound in a model extraction solution

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ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 12 June 2014
Accepted 13 June 2014
Available online 20 June 2014

Keywords:
Change
Gallic acid
Ultrasound
Extraction
Degradation

ABSTRACT

Ultrasound has been widely used as a new kind of auxiliary extraction technique in food industry, but its effect cannot be ignored on the potential degradation of the extracted target compound. In this paper, a model extraction solution was constructed with the standard gallic acid as target compound to be extracted, and its change was monitored by using high performance liquid chromatography (HPLC) under different ultrasonic extraction conditions, namely, solvent types, extractant concentrations, extraction time, extraction temperature, ultrasound power and frequency, in order to understand the effect of ultrasound on the extract during ultrasonic extraction and provide an objective evaluation of ultrasonic extraction of polyphenols. The results indicate that ultrasonic parameters had definite effect on the degradation of gallic acid during ultrasonic extraction, which implies that the extraction yield should not be over-focused in actual extraction applications of ultrasound, more attention should be paid to the potential degradation of the extracted target compound induced by ultrasound.

1. Introduction

Compared to conventional extraction techniques, ultrasound-assisted extraction (UAE) provides an inexpensive, less time consuming, environmentally friendly and efficient method and is considered to have a promising potential application in extraction field. Using ultrasound at the frequency of 20–100 kHz, full reproducible food processes can now be completed in seconds or minutes with high reproducibility, simplifying manipulation and work-up scale, eliminating post-treatment of waste water, reducing solvent consumption and energy input [1–4]. As a novel technology, UAE has attracted much more attention and is widely used in the fields of separation and extraction in recent years. It has already been reported successfully applied in the extraction of natural products, such as the extraction of antioxidant compounds [5], phillyrin [6], polysaccharides [7], polyphenols [8], eight ginsenosides [9], flavonoids [10], betulin [3], vanillin [11], phenolics [12], carotenoids [13], etc.

Generally speaking, the mechanism of UAE is attributed to cavitation, mechanical, and thermal effects which can destroy cell walls, reduce particle size, and enhance mass transfer [14]. The enhancement in extraction efficacy using ultrasound is mainly due to the effect of acoustic cavitations produced in the solution by the propagation of ultrasound wave [15,16]. Furthermore, ultrasonic irradiation also can cause greater penetration of solvent into the sample matrix through the effect of mechanical, improving the contact surface area between the solid and liquid phase, and as a result, the target compounds more rapidly diffuse from the solid phase into the solvent [17,18]. To be specific, after the interaction of ultrasonic waves with the subjected plant material during extraction, their physical and chemical properties altered, and the release of extractable compounds and the mass transfer are accelerated by the ultrasonic cavitational effect on the disrupting of the plant cell walls [19].

In other words, great attention has been paid on the mechanical or physical aspect to explain the mechanism of UAE. In most cases, only some variables (e.g., temperature, time contact, solvent-to-solid ratio, particle sizes, etc.) which would influence the extraction yield or efficiency are studied or optimized regarding ultrasonic extraction, and many of such studies are focused on parametric and kinetic analyses of extracts [5,20,21], and comparison of extraction efficiencies with those conducted in the absence of ultrasound [11], while its physical and chemical effects on the degradation of target compounds are often ignored, and which is the exact what we are concerning.

Acoustic cavitation is generally defined as the formation, subsequent growth, shrink and implosive collapse of bubbles in the liquid under the effect of ultrasonic, resulting in very high local energy densities [22]. The collapse of cavitation bubbles produces

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http://dx.doi.org/10.1016/j.ultsonch.2014.06.010
1350-4177/

very high instant local temperatures (>5000 °C), pressures (>1000 atm), and electrical charges as well as plasma effects, leading to enormous heating and cooling rates (>109 k/s) [23,24], which can results in intensification of chemical reactions and physical effects [25]. In addition, cavitation can also lead to strong acoustic streaming, high shear stress around the bubble wall, formation of micro-jets near the solid surface and generation of highly active free radicals, which can result in the degradation of the compounds [22]. Attributed to the cavitational effects, the organic compounds can react with reactive radicals generated in aqueous solution either inside the bubble, at the liquid-bubble interface or in the liquid bulk depending on the nature of the solute and result in a degradation [26]. Furthermore, the effects of acoustic cavitation generated by ultrasound has been successfully used for degradation of several compounds such as formic acid [27], phenol [28,29], 2,4-dinitrophenol [30], dimethyl phthalate [31], 2-chlorophenol [32], p-nitrophenol [33], methylene blue [34], *m*-xylene [35], etc. Gogate [36] has given an excellent review on the mechanism of cavitation based process intensification and made a theoretical analysis of sonochemical degradation of phenol and its chloro-derivatives [37], which was highly worth considering in the UAE applications. In a word, the sonochemical effect should be noted in ultrasonic extraction field. Recently, several researches which describe the application of sonochemical techniques to aqueous systems to remove phenol and phenolic compounds have been widely investigated with emphasis on the identification and optimization of operating parameters such as frequency, pH, dissolved gases, reactor geometry and the type of chemical reagents and catalysts [38–40]. One point that should be emphasized is that the ultrasonic parameters in wastewater treatment are a bit different with those used in UAE. Specifically, the frequency and the power empolyed in the former are higher than those in the latter. To the best of our knowledge, a few studies have reported the potential destruction of the extracted target mediated by ultrasonic waves during UAE. Based on these considerations, a study was designed to evaluate the effect of ultrasonic parameters (solvent, time, temperature, extractant concentrations, frequency and power) on the stability of the extracts in a model extraction solution subjected to ultrasonic waves. Considering the fact that phenol is one of the most common extracted targets in industrial production, gallic acid is employed as the typical phenolic compound so as to simplify the procedure in this paper.

2. Materials and methods

2.1. Materials and reagents

Gallic acid was obtained from Alfa Aesar Chemical Co., Ltd (China). Methanol, ethanol, acetone and acetic acid glacial of analytical grade were purchased from Xi'an Chemical Co., Ltd (Shanxi, China). Methanol of HPLC grade was purchased from Tedia Company, Inc. (USA). Deionised water was used throughout the experiment (obtained through a Millipore filter system, Millipore Co., Ltd, MA, USA). All other organic solvents used in the study were of analytical grade.

An ultrasonic cleaner was used as an ultrasound source in this study. The cleaner, KQ-300VDE (Kunshan ultrasonic instrument Co., Ltd, Jiangsu, China), was basically a rectangular container, to which six transducers were annealed at the bottom, its maximum power output is 300 W, its temperature can be self-controlled, and three frequencies of 45, 80, and 100 kHz can be chosen.

2.2. Experimental designs

The following variables were examined by using one factor experiment design to investigate the effects of ultrasound treatment on the gallic acid including solvents (methanol, ethanol, and acetone), extractant concentration (30%, 40%, 50%, 60% and 70%, mL/mL), ultrasonic power (120, 180, 240 and 300 W), ultrasonic frequency (45, 80 and 100 kHz), temperature (30, 40, 50, 60, 70 and 80 °C), and time (15, 30, 45, 60, 75, 90, 105 and 120 min), respectively. The original concentration of gallic acid was 100 μg/mL in all the experiments. After ultrasonic treatment, the residual content of the gallic acid was calculated according to the peak area obtained by high performance liquid chromatography against the standard curve which was constructed by plotting peak areas against the concentrations of standard gallic acid. To be specific, the standard curve was constructed by the following procedures: a series of concentrations of gallic acid solution (0, 20, 40, 60, 80, and 100 μg/mL) was prepared, of which 10 μL was taken out and then injected into the HPLC which worked under the following conditions in the Section 2.3. Thereafter, the standard curve was regressed between the concentrations of gallic acid and its corresponding peak areas recorded by HPLC.

2.3. HPLC analysis

HPLC analysis was performed using a Waters HPLC system, which consists of a model 1525 binary HPLC pump (Waters, Milford, MA) equipped with a Rheodyne injector (loop, 20 μL) connected with a model 2996 photodiode array detector (Waters). Samples were separated on a TC-C_{18} column (5 μm, 4.6 mm × 250 mm, Agilent, USA) and chromatograms were analyzed by the Empower software (Waters). All mobile phases for the chromatographic analysis were filtrated through a 0.45 μm membrane and ultrasonically degassed for 20 min prior to use. The HPLC working parameters were as follows: flow rate 1.0 mL/min, column temperature 30 °C, injection volume 10 μL and mobile phase A (methanol containing 1% glacial acetic acid) and B (H_2O containing 1% glacial acetic acid acid). The gradient program was: 0–20 min from 15% to 100% of mobile phase A, 20–25 min of 100–15% at the flow rate of 1 mL/min. The PDA detector was set at the wavelength of 270 nm.

3. Results and discussion

3.1. Effect of ultrasonic solvent types on the stability of gallic acid

In order to investigate the effect of different solvents on the stability of gallic acid under the treatment of ultrasound, the used extractants were methanol, ethanol and acetone, respectively. The working parameters of ultrasound were at the frequency of 100 kHz, power of 120 W, time of 30 min, temperature of 23 ± 1 °C and extractant concentration of 60% (mL/mL). In addition, the standard curve was demonstrated by the regress equation of $y = 32514x - 80839$ with a correlated coefficient of 0.9971 ($n = 6$), which means that there was a good linear relationship between the peak areas and concentrations within the range of gallic acid from 0.00 to 100.00 g/mL. Therefore, the changes of gallic acid could be quantified according to constructed curve in the following studies.

The remaining weight of gallic acid after ultrasonic treatment was shown in Fig. 1. Specifically, the highest degradation rate of gallic acid happened in the methanol solution when subjected to ultrasonic waves, while the lowest happened in the ethanol solution, and interestingly ethanol is the extractant frequently used in extraction industry and the reason why ethanol is always used as the solvent may be explained by the results in this study.

The lower degradation rate of gallic acid in ethanol under ultrasonic treatment in comparison of methanol and acetone may be due to its liquid phase physicochemical properties under the