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The kinetics of extraction of the medicinal ginger bioactive compounds using hot compressed water

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ABSTRACT

Zingiber officinale or ginger known for its high medicinal compounds is extracted using hot compressed water (HCW). The two most important bioactive compounds namely 6-gingerol and 6-shogaol in the ginger extracts are analyzed using HPLC. The effects of temperature and time of extraction on 6-gingerol and 6-shogaol are studied using HCW extraction. It is found that HCW extraction can extract these two bioactive compounds; 6-gingerol at 130 °C and 30 min whilst 6-shogaol at 170 °C and 20 min. This finding shows that HCW extraction is potentially used in selective extraction of bioactive compounds at different conditions of HCW. The kinetics of extraction for both bioactive compounds is studied from the optimum temperatures obtained. The overall mass transfer coefficient which represents the extraction efficiency is calculated using mass transfer model. The optimum values of the overall mass transfer coefficient (k) for 6-gingerol is 8×10^{-7} m/s at 130 °C whilst for 6-shogaol, is 18×10^{-7} m/s at 170 °C using HCW extraction. The relationship between the overall mass transfer coefficient and the dielectric constant of various solvents for 6-gingerol is identified. Similar relationship is identified for 6-shogaol using HCW as solvent. The dielectric constant does not contribute to the extraction efficiency of 6-gingerol and 6-shogaol.

1. Introduction

Ginger or *zingiber officinale* is known to be anticancer [1,2], antioxidants [2] and anticarcinogenic [3]. The main bioactive compounds that exhibit these medicinal properties are the series of gingerols, shogaol and paradol. The most important medicinal compounds identified are 6-gingerol, 10-gingerol and 6-shogaol. 6-Gingerol, the most abundant compound in ginger rhizome has been proven to give positive response in mediating cardiac contractile, act as antioxidant [4], antiproliferative and also apoptosis [2]. 10-Gingerol has significant medicinal effect such as antibacterial [5] and antimicrobial activities [6]. 6-Shogaol is another predominant pungent constituent in ginger is proven to reduce cell death and restores motor function in rat spinal cord injury [7] and lessen the human oral cancer [8]. Furthermore, pharmacokinetics study of 6-gingerol, 10-gingerol, and 6-shogaol shows that all these compounds are absorbed quickly in the serum with majority detected as glucuronide metabolites [9].

The proven medicinal roles of each ginger compound have promoted the search for selective extraction to give an added value to the ginger oleoresin. Ginger in its fresh form is made up of isolated cells containing oleoresins comprising of gingerols and shogaols [10]. In dried ginger, the oleoresin cell wall is ruptured and exposed. This can facilitate the extraction of ginger bioactive compounds.

The use of water in subcritical region as a 'green' solvent has attracted the interest of numerous researchers from all over the world. Thermodynamically, water in its liquid state below the critical point of 374 °C and 22 MPa is referred to as subcritical water. Meanwhile, hot compressed water (HCW) specifically refers to subcritical water above the normal boiling point of 100 °C [11]. HCW extraction has been successfully utilized for herbal extraction as demonstrated in the extraction of cumin [12], zataria multiflora [13], centella asiatica [14], thymbra spicata [15], bitter melon [16] and oregano [17].

HCW does not only act as a 'green' solvent but it also has the potential use for selective extraction [18]. Wiboonsirikul and Adachi have reported that the main parameters that affect the extraction

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efficiency during HCW extraction process are temperature and time [19]. Meanwhile, pressure is proven to have no significant effect on the extraction efficiency [17]. The effect of temperature and time for the extraction of 6-gingerol and 6-shogaol from *zingiber officinale* using HCW are explored in this study for the potential use in selective extraction.

There is no known mass transfer data available for 6-gingerol and 6-shogaol which is required for design purposes in particular for the optimization of HCW extraction process. The overall mass transfer model is applied to 6-gingerol and 6-shagaol extraction using HCW to determine the overall mass transfer coefficient, k. The k value represents the extraction efficiency of a process. The k value is affected by the properties of the solute as well as the solvent. The dielectric constant is a fundamental property of a solvent and it has been shown that it is affected significantly by temperature and insignificantly by pressure [20]. Dielectric constant varies with different types of solvent and generally, organic solvents such as hexane, acetone and chloroform have lower dielectric constants which increase the solubility of organic solutes. The relationship between the dielectric constant of different types of solvent on extraction efficiency of 6-gingerol is confirmed in a study by Shadmani et al. [21]. The effect of the dielectric constant of HCW on the k value of 6-gingerol and 6-shogaol is investigated in this study.

2. Material and method

2.1. Material

Dried and ground ginger was supplied by a local supplier from Ranau, Sabah, East Malaysia. The ginger standards of 6-gingerol (85.8% w/w), 10-gingerol (95.1% w/w) and 6-shogaol (96.4% w/w) were purchased from ChromoDex Inc., CA, USA. Acetonitrile and methanol were of High Performance Liquid Chromatography (HPLC) grade, supplied by MERCK, Germany. Distilled water was used in the HCW extraction.

2.2. Hot compressed water extraction

HCW extraction was done batch wisely using the fabricated equipment in this laboratory as shown in Fig. 1. Prior to this, preliminary experiments on temperature effect were done using 32 ml extraction cell of Accelerated solvent extractor (ASE 200, Dionex, USA) to verify the result of the fabricated equipment. The solvent of sample ratio used in this equipment was scaled up from the ASE as recommended by the manufacturer. The fabricated equipment consisted of two vessels with one liter volume each; the extraction and the cooling cells connected by a ¼ in. stainless steel pipeline. 75 g of ground ginger was weighed and loaded into a covered stainless steel mesh cylinder before being placed into the extraction cell. 700 ml of distilled water was added into the cell. The cell was then securely covered with a stainless steel lid. N_2 gas was then passed through the cell for 2 min to purge out air and dissolved oxygen. Excess pressure was relieved through the release valve. The temperature was set according to the required experiment. The electrically jacketed extraction cell took 3–5 min to achieve the desired temperature. The extraction time started once the set temperature was achieved as indicated by the temperature indicator in the extraction cell.

The effect of temperature was studied independently from 100 to 200 °C with 10 °C increment and referred to as the first set of experiments. The extraction time was kept constantly at 30 min. For example, at 100 °C, the first experiment in the first set was run for 30 min, the second experiment was run at 110 °C for 30 min and so on up to 200 °C for 30 min, which the temperature increased but the time was constant.

The effect of extraction time was studied at 10, 20, 30, 40, 50 and 60 min at the determined optimum temperature from the temperature effect experiment and referred to as the second set of experiments. For example, if the optimum temperature for 6-gingerol was T1, the first experiment in the second set was T1 for 10 min, the second experiment was run at T1 for 20 min and so on up to 60 min at T1. All experiments were carried out at constant pressure of 3.5 MPa. Once the extraction process was completed, the extractant was transferred into the cooling cell at 25 °C and 1 MPa within 1 min to ensure rapid cooling.

Ginger extracts were collected and subjected to further analysis using HPLC. Each experimental condition was run triplicate. The average absolute deviation, AAD was applied for each set of experiment using Eq. (1).

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{n}\frac{|x_i - \bar{x}|}{x_i} \tag{1}$$

where i, n is the no. of runs for one experimental condition; N the total no. of runs; x_i the data for one experimental condition; $\bar{x}$ is the average for one experimental condition.

The percent recovery of each bioactive compound was calculated using Eq. (2).

$$\text{Percent recovery} = \frac{c_i \frac{\mu\text{g bioactive}}{\text{g dried ginger}}}{c_{o_i}, \frac{\mu\text{g bioactive}}{\text{g dried ginger}}} \times 100 \tag{2}$$

where c_i is the species concentration in the bulk solution; c_{o_i} is the species initial concentration obtained using eight hours soxhlet extraction with ethanol.

2.3. HPLC analysis for ginger bioactive compounds

The analysis were carried out using HPLC (Waters Corp., MA, USA) equipped with Photodiode Array (PDA) detector and the Lichrocart 250-4, 6 Purospher Star RP-8E (5 Mym) column (MERCK, Germany). In this analysis, 10 min run time was used with 8 min as an injection delay. Two mobile phase solutions were used which were A; 100% acetonitrile and B; 65% (v/v) methanol in water. The mobile phase ratio A to B increased gradually during the separation process from 20:80 to 50:50 (volume of A/volume of B) at a constant flow rate of 1.20 ml/min. 10 µl of sample extracts were

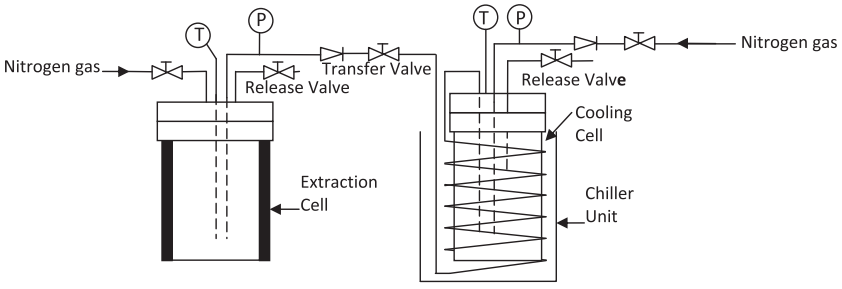

Fig. 1. Schematic diagram of HCW extraction facility.