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Temperature effects on diffusion coefficient for 6-gingerol and 6-shogaol in subcritical water extraction

Nor Ilia Anisa [1, 2], Noor Azian [1, 2,*], Mohd Sharizan [1, 2], Yoshio Iwai[3]
[1]Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, 54000 Kuala Lumpur, Malaysia
[2]Center of Lipids Engineering and Applied Research (CLEAR), Universiti Teknologi Malaysia, 54000 Kuala Lumpur, Malaysia
[3]Department of Chemical Systems and Engineering, Kyushu University, Fukuoka 812-8581, Japan

E-mail: azian.morad@gmail.com

Abstract. 6-gingerol and 6-shogaol are the main constituents as anti-inflammatory or bioactive compounds from zingiber *officinale* Roscoe. These bioactive compounds have been proven for inflammatory disease, antioxidatives and anticancer. The effect of temperature on diffusion coefficient for 6-gingerol and 6-shogaol were studied in subcritical water extraction. The diffusion coefficient was determined by Fick's second law. By neglecting external mass transfer and solid particle in spherical form, a linear portion of Ln (1-(Ct/Co)) versus time was plotted in determining the diffusion coefficient. 6-gingerol obtained the higher yield at 130^{o}C with diffusion coefficient of 8.582x10^{-11} m^2/s whilst for 6-shogaol, the higher yield and diffusion coefficient at 170^{o}C and 19.417 x 10^{-11} m^2/s.

1. Introduction

Ginger, the rhizome of Zingiber officinale is one of widely used species of the zingiber family (zingibereace) and is common used for various foods and beverages. Oleoresin (extract crude) has medicine values. The oleoresin of ginger contains the pungent and non-pungent constituents, also in addition to the volatile oil [1]. The major constituent of ginger is lipophilic rhizome extracts, have yielded potentially to active gingerols. The substances which are phenolic ketones are responsible for the pungent flavour of fresh ginger and known as; 4-, 6-, 8-, 10-, and 12-gingerol. During thermal processing or storage, the gingerols may be modified to a series of homologous compounds known as shogaols (8- and 10-shogaols). These gingerols and shogaols had been reported to possess the following activities; anti-inflammatory disease [2], antioxidatives [3] and anticancer [4].

Subcritical water extraction (SWE) is an alternative method on extraction the plant for pharmaceutical proposes since this method deals with the usage of water only. The SWE is operating at elevated temperature; above than boiling point to near critical point of water (100-374^{o}C) at moderate pressure for maintain the water in liquid state. From Mustafa and Turner [5], the principle of green technology is to reduce the using of harsh organic solvent whilst encourage the use of novel extraction technique that are known to be more friendly. Indeed, SWE is direct method to recover the solutes without using the stage of clean-up which have advantages in time consuming and cost reduction [6].

Knowledge of mechanisms and kinetic study on extracting the solutes or compounds from natural plant matrix is crucial for optimizing the design and operating conditions. Indeed, the estimation of diffusion coefficient is important to determine the rate of mass transfer in extracting solutes from solid matrix [7]. Thus, in obtaining the optimum yield of extraction the bioactive compounds or solute from natural plant, the mechanisms of extraction should be well understood. In describing mechanism of extraction, the first step (1) is desorption of solute through the stagnant film layer into the solid plant matrix. This step may be dominated by the adhesive and cohesive forces

between solid plant matrix, solvent and solute. The less bound solute is more easily dissolved into the solvent [8]. The second step (2) is the diffusivity of solvent into the solid plant matrix which this step involve the breaking of chemical bonds within the solid plant matrix. The third step (3) is dissolution of solutes into the bulk solvent due to concentration gradient and may be described by the partitioning equilibrium. The solubility of solutes in solvent will depends on the polarities of desired solutes and solvent. The last step (4) is elution or removal of the solutes from solid plant matrix through stagnant solvent [9, 10, and 11]. A mathematical model based on Fick's second law which introduced by Crank [12] describes the extraction process.

Thus, it is obvious that diffusivity of solute in a solvent plays a major role in describing mechanism of extraction. Diffusivity of solute also varies with process temperature. This study investigates the temperature effects on diffusivity for the ginger bioactives 6-gingerol and 6-shogaol.

2. Material and methods

2.1Material and methods

Dried and ground zingiber officinale Roscoe samples were obtained from local supplier. The mean particle size of 1.59 mm was obtained.

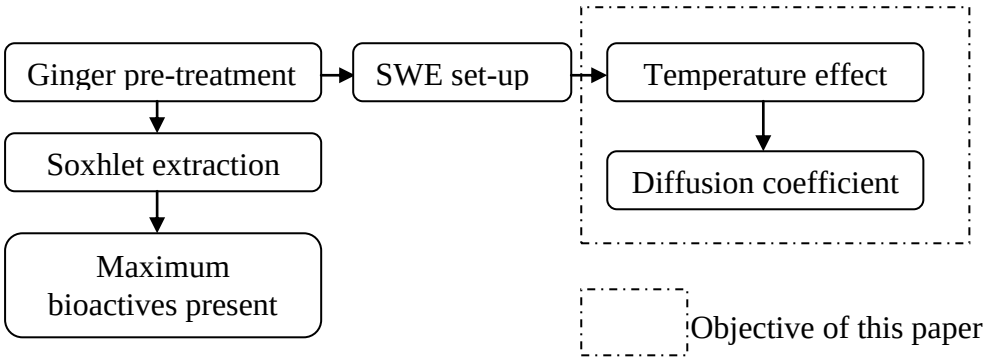


Figure 1. Overall research methodology

2.2Subcritical water extraction (SWE) CLEAR prototype

The SWE with 1L capacity was used in extraction process. Ratio of ginger to water was 1:10 with constant pressure at 3.5MPs and was operated in cumulative process within 60 minutes. The fresh solvent was introduced for each 10 minutes during the extraction process as stated by Sharizan [13].

2.3Soxhlet extraction

70g of dried and ground ginger was weighed and extracted with 280mL of ethanol for 8 hrs using soxhlet extraction apparatus. The extraction temperature was constant at the boiling point of ethanol (78.1^{o}C) and monitored using infrared laser thermometer (AR300, China). The process is repeated for each prescribed time. Then, the extracted sample was purified in rotary evaporator (Buchi R-205, Switzerland) to remove the ethanol. The experiments were conducted in triplicate and standard deviations were calculated (<5%).

2.4 HPLC analysis

The HPLC (Waters 600-MS, USA) equipped with Photo iodide Array Detector (Waters, USA). The method of this analysis was adapted by Sharizan [13] as follows: mobile phases flow rate; 1.2 ml/min;

column temperature; 35-38oC; chromatographic run; 20 min; eluents: (A) acetonitrile and (B) water. The percentage of the solvent A to solvent B was increased gradually from 20 % to 50 %.

2.5 Diffusion Coefficient

From [12], the diffusion coefficient is described by Fick's second law;

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right), \text{ for multidirectional diffusion} \quad (1)$$

By assuming (i) the ginger matrix is uniformly in a spherical form, (ii) there is no interaction between the bioactives, (iii) the diffusivity of the extracted bioactives is constant, thus the initial and boundary conditions are obtained as follows:-

Initial condition $C_{(t=0)} = C_i$

Boundary conditions $C_{(r=r_b)} = 0$

$\partial C_{(r=r_c)} / \partial r = 0$

where r is radial distance coordinate from centre of spherical particle (m), r_b is radius of spherical particle and r_c is centre of spherical particle (r=0).

By considering the diffusivity is constant in one-direction, the equation is given by:-

$$\frac{\partial C}{\partial t} = \frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) \quad (2)$$

The content of solutes in solid varies with time and distance. The diffusion coefficient of solutes can be determined through the concentration changes of solutes in respect solvent with time:-

$$\frac{C_t}{C_o} = \frac{4r}{\pi}\sum_{n=1}^{\infty}\frac{1-(-1)^n}{n.\pi}\exp\left(-\frac{n^2\pi^2}{r^2}.D_e t\right) \quad (3)$$

where C_t and C_o are the concentration at time given (μg/g) and concentration of bioactives in solid (μg/g). *De* is diffusion coefficient (m^2/s) of solute in subcritical water and average radius of solid matrix (m).

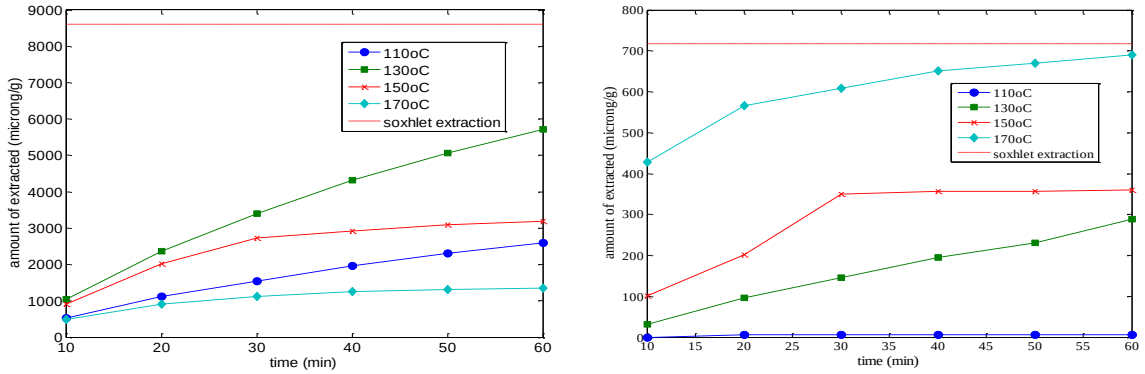
For sufficiently prolonged tine, truncating it to the first term in the Eq. (3) can obtain [14]:-

$$1 - \frac{C_t}{C_o} = \frac{6}{\pi^2}\exp\left(-\frac{D_e \pi^2 t}{r^2}\right) \quad (4)$$

D_e could be determined from the slope (D_e= slope x r^2/π^2) of the linear portion of *Ln (1-(Ct/Co))* versus time.

3. Results and discussion

The effect of temperature on the extracted yield was determined for the temperature ranges of 110 to 170°C for both 6-gingerol and 6-shogaol as shown in Figure 2 (a) and (b), respectively. The maximum yield of 6-gingerol and 6-shogaol is determined through soxhlet extraction using ethanol as solvent are 8406.996 µg/g and 716.76 µg/g, respectively. 6-shogaol using SWE was found to be 690.401 µg/g at 170°C and this approaches the maximum yield of 716.76 µg/g or 96% yield as depicted in Figure 2 (b). This phenomena is due to the hydrolysis of 6-gingerol to 6-shogaol at higher temperature [15].



(a) (b)

Figure 2. The bioactive compounds extract a) 6-gingerol b) 6-shogaol

Referring to Figure 2 (a), the trends of extraction process at 150 and 170°C are classified by three stages; rapid, transition and constant extraction process. The rapid extraction stage occurred up to 20 minutes and in this stage it involves the 'free solutes' or 'easy accessible' solutes from solid matrix to the bulk solvent. The transition stage involves the depletion of the 'free solutes' from solid matrix from 20 to 30 minutes. The 6-gingerol reached the third stage (constant extraction process) within 30 minutes. While at lower temperature conditions, there is no indication of three stages of extraction process taking place. The extraction process occurs in two stages for the temperature of 110 and 130°C.

As referring to Figure 2 (b), at 110°C there was no significant of 6-shogaol observed. This is due to the higher of 6-gingerol present and the dehydration of 6-gingerol to 6-shogaol is slower at this temperature. Meanwhile at 150°C, trend of extraction process was analogous to the trend of 6-gingerol at 150 and 170°C. Thus, the extraction process also can be described by three stages; rapid, transition and constant. As mentioned for 6-gingerol, the stages are involving the 'tied solute' and 'free solutes' to be dissolved in bulk solvent. However, at 130°C, the extraction process of 6-shogaol was not high enough to observe the 'tied solutes'. This is might be the 'free solute' was dissolved in bulk solvent and the remaining solute was still in solid matrix. The highest yield which reached the maximum amount of 6-shogaol presents was observed at 170°C. From the figure, there were two stages of extraction process, but it would be changed to three stages at longer extraction time.

The stages of extraction process in Figure 2 are important to be investigated for optimisation and cost reduction of operating. Once the constant extraction process is achieved, the extraction process should be stopped.

A linear line is not appropriate when plotting *Ln (1-(Ct/Co))* versus time at higher temperature (150 and 170°C) as shown in Figure 3. This phenomenon can be explained from the remaining of solutes (6-gingerol and 6-shogaol) in the solid matrix (zingiber). At higher temperatures, water can diffuses more into the solutes, thus tends to dissolve the solute due to higher mass transfer rate and reduction of driving force.

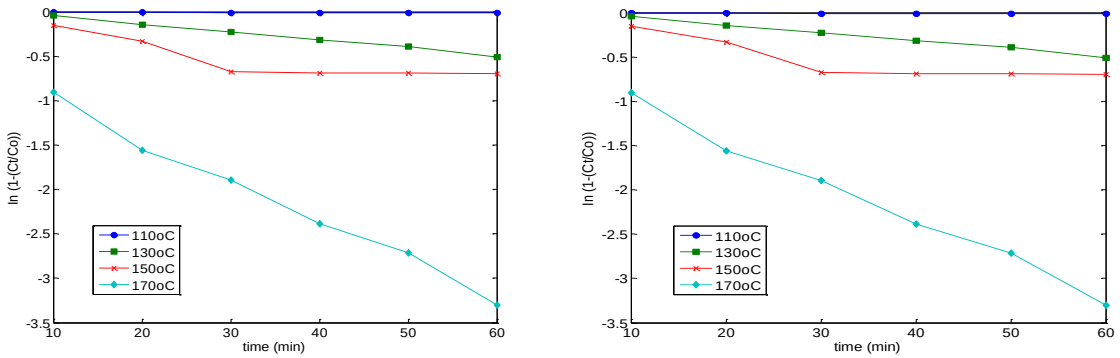


Figure 3. Prediction of diffusion coefficient for (a) 6-gingerol and (b) 6-shogaol

Table 1 shows the calculated diffusion coefficient, D_e increased from 0.427×10^{-11} m^2/s to $19.417 \times 10^{-11} m^2/s$ ascending with temperature. This is consistent with the findings by Ho et al. [17], who showed that the diffusion coefficient in extraction of lignans from flaxseed meal increased with temperature because of the enhancement in extraction rates and mass transfer of solutes from solid matrix. However, the diffusion coefficient of 6-gingerol did not obtained the similar trend. The diffusion coefficient for 6-gingerol is highest at 130°C was 2.903×10^{-11} m^2/s and drastically reduced to 0.940×10^{-11} m^2/s at 170°C. 6-shogaol is more lipophilic than 6-gingerol, thus at higher temperature the loss of a hydroxyl group from 6-gingerol to 6-shogaol is due to dehydration as mentioned earlier [15].

Table 1. Diffusion coefficient of 6-gingerol and 6-shogaol with respect to temperature

Temperature (°C)	Diffusion coefficient, $D_e \times 10^{11}$ (m^2/s)	
	6-gingerol	6-shogaol
110	2.605	0.427
130	8.582	3.885
150	2.903	4.653
170	0.940	19.417

Karacabey et al. [18] have reported that calculated diffusion coefficients of trans-resveratrol were increased from 3.3 to 10.4 x 10^{-11} m^2/s with ascending temperature from 105 to 160°C. However as comparing to the 6-gingerol, the results did not indicated the same trend. This is because of 6-gingerol do not stable as the other compounds studied. The properties of bioactive compounds also play a role on the effectiveness of diffusivity. According to the LeBas equation, the molar volumes of 6-gingerol and 6-shogaol are 377.4 and 363.6 cc/mol, respectively. The diffusivity of solutes will be higher at lower molar volume pointing to 6-shogaol having a higher diffusivity compared to 6-gingerol [16].

4. Conclusion

For SWE, it was identified that the optimum temperature conditions were 130°C and 170°C for 6-gingerol and 6-shogaol, respectively. Diffusion coefficient is the highest at these temperatures; 8.582 x 10^{-11} m^2/s for 6-gingerol and 19.417 x 10^{-11} m^2/s for 6-shogaol. Thus, the yield of extraction also was correlated to the diffusion coefficient. Since the studies of diffusivity in subcritical water extraction is still rare, the diffusivity model ignored the external mass transfer resistance. In future, the comparison of external and non-external mass transfer resistance should be considered to improve the knowledge and findings in diffusivity of bioactives.

5. Acknowledgements
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References
[1] Azian M N *et al* 2010 *Journal of Food Engineering* **62** 359–364
[2] Lee S W *et al* 2011 *Food Chemistry* **128** 78–782
[3] Sang S *et al* 2009 *J Agric Food Chem*. **57** 10645–10650
[4] Harliansyah *et al* 2007 *Asian Journal of Biochemistry* **2** 421-426
[5] Mustafa A and Turner C 2011 *Analytica Chimica Acta* **708** 8-18
[6] Teo C C et al 2010 *Journal of Chromatography A* **1217** 2484–2494
[7] Varzakas T H *et al* 2005 *Enzyme and Microbial Technology* **37** 29-41
[8] Carr A G *et al* 2011 *Chemical Engineering Journal* **172** 1-17
[9] Anekpankul T *et al* 2007 *Separation and Purification Technology* **55** 343–349
[10] Waldebäck M *Pressurized Fluid Extraction. A sustainable technique with added values*. Uppsala, Acta Universitatis Upsaliensis, 2005.
[11] Islam M Z *et al* 2013 *Journal of Industrial and Engineering Chemistry* **19** 129–136
[12] Crank J *The mathematics of diffusion*, Oxford University Press, Oxford, 1975
[13] Sharizan M M S *Subcritical water extraction of 6-gingerol and 6-shogaol from Zingiber Officinale*. Msc Thesis, Universiti Teknologi Malaysia, 2012
[14] Cussler E L *Diffusion: Mass transfer in fluid systems*. Cambridge University Press, New York: USA; 1984
[15] Guerrero M S et al 2008 *Bioresource Technology* **99** 1311-1318
[16] Bhattarai S T et al 2001 *Journal of Pharmaceutical Sciences* **90** 1658-1664.
[17] Ho et al 2008 *Journal of Food Engineering* **89** 64-71
[18] Karacabey et al 2012 Food Bioprocess Technol **5** 359-371