Mass Transfer Coefficient Study of Shogaol Extraction in Ginger Using Subcritical Water

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Abstract. Ginger (Zingiber officinale) has bioactive components such as shogaol and zingerone which are able to mediate cardiac contractions, are antioxidant, antiproliferative and apoptosis. To increase the economic value, it is necessary to develop a process of extracting ginger active compounds through subcritical water. The superiority of hydrothermal extraction by using water is easy to get, cheap, abundant availability, high purity, non-toxic and easy to handle. This study aims to obtain data on the mass transfer coefficient of the extraction process of ginger bioactive compounds such as shogaol through subcritical water. These data are very much needed in the design and scale-up of the extractor tool. The results of the study show that hydrothermal extraction using subcritical water can increase the content of Shogaol compounds, compared to conventional extraction processes such as soxhletation, percolation, supercritical fluid extraction, microwave extraction, and ultrasonic extraction. Mass transfer coefficient (Km) in the model mass transfer extraction of shogaol, ginger using subcritical water respectively 3,7503 s⁻¹, 3,6912 s⁻¹, 0.31435 s⁻¹.

1. Introduction

The need for raw materials for national drug production in Indonesia, 90% is still met through imports with a value reaching 11.4 trillion in 2018 [1]. Efforts to increase independence in the health sector include developing the production of medicines and raw materials based on Indonesia's biodiversity plant diversity [2] [3]. Ginger (Zingiber officinale) which is one of the medicinal plants is known to have various pharmacological effects such as anticancer, antioxidant, anti-carcinogenic and antiosteoporosis [4] [5]. The main bioactive components of ginger that show pharmacological properties include shogaol, and zingerone [6] [7] [8] [9] [10].

Although 6-gingerol and 6-shogaol have similar chemical structures, and both are known to have beneficial bioactive properties, 6-shogaol has a stronger active power. Numerous studies have shown that 6-shogaol has greater effectiveness than 6-gingerol in many cases, such as in antioxidant activity [8] [11] [12] [13], anti-inflammatory activity [8] [14] [15], anti-platelet aggregation effect [16], inhibits muscle contraction [17] [18], inhibiting colorectal cancer [14], ovarian cancer [19] [20], breast cancer [21], and lung cancer [22] [23].

Therefore, efforts are needed to develop 6-shogaol production through the 6-gingerol extraction and conversion process. The development of the 6 shogaol extraction process resulting from 6-gingerol conversion can be done through several separation techniques, including: (i) soxhletation [24], (ii) subcritical extraction [25], (iii) supercritical fluid extraction [26], (iv) hydrotropic extraction [27], (v) microwave extraction [27] [28], (vi) enzymatic extraction [29], (vii) ultrasonic extraction [30] [31], and ionic liquid extraction [32]. The extraction process is carried out using various solvents such as ethanol, methanol, acetone, dichloromethane, hexane, water, CO₂ and 1-decyl-3-methylimidazolium bromide.
This research was conducted to determine the effect of time to shogaol mass transfer into the subcritical water phase.

2. Methods

2.1. Study of Mass Transfer Events and Computational Processes

The modeling activity begins by compiling a mathematical equation about the mass transfer events of the bioactive compound from the feed phase to the solvent phase which may be based on theoretical studies and based on many previous studies, which were carried out at the Laboratory of Chemical Engineering Process Computation at Diponegoro University Vocational School Semarang. The model is made based on the theory of mass transfer at 1 stage extraction. The postulated model is then derived to obtain an equation which will later be tested using data obtained from the experimental.

Experiments were conducted to obtain data that are useful in determining the extraction rate coefficient parameters that are modeled in empirical equations. The data that has been measured is used as a tool to validate the postulations that have been set. Data measurements were carried out at the Laboratory of Chemical Engineering Operations at the Diponegoro University Vocational School. Thus, validated models and empirical equations will be obtained.

Research materials in the form of wet ginger, nitrogen, and chemicals needed to support the hydrothermal extraction process such as N₂. Materials for product analysis include: acetonitrile, nitrogen, methanol, phosphate buffer, ethanol, distilled water, sodium hydroxide, potassium hydroxide, hydrochloric acid and phenolphthalein indicators. The main ingredients for the research are ginger rhizomes from the banyumanik market and ginger farmers in Tembalang District, Semarang. Chemicals bought at CV. Juru Maju Semarang. Standard Shogaol and are buy from Sigma.

The main tool that will be used in this research is the hydrothermal extractor unit. While the supporting tools that will be used for analysis include centrifugation, magnetic stirrers, burette analytical balance, with a volume of 10 ml and a scale of 0.02, pycnometer, with a volume of 5 ml, viscosimeter, Erlenmeyer, with a volume of 250 ml, volume pipette, with volume 10 ml, beaker glass, with a volume of 500 ml and 100 ml, pipette drops, and papa capillaries.

The research variables varied were temperature, solvent-feed ratio, extractor pressure and extraction time. Extractor temperature is set at 130, 140, 150, 160, 170, and 180°C because it is a temperature range with perfect solubility of shogaol to the subcritical solvent phase. Feed solvent ratios are set at 1: 1, 2: 1, 3: 1, 4: 1 and 5: 1. The extractor pressure is set at 2, 2.5, 3, 3.5 and 4 MPa. The extraction time is set at 10, 20, 30 and 40 minutes.

The ginger rhizome is cleaned of dirt and grinded to get the size of the powder. 75 g of ginger powder, put into a stainless tube with a lid and put into extraction cells. 700 ml of distilled water and varied to a certain ratio were added to the cell. The cell is closed with a stainless lid, N₂ gas is liquefied into the cell for 2 minutes to remove air and dissolved oxygen. The excess pressure is discharged through the valve. The temperature is set under certain conditions and heating takes 3-5 minutes to reach the desired temperature. The extraction process starts (t = 0) when the temperature is reached under certain conditions. All experiments are carried out under certain pressure. After the process is complete, the extractant is transferred to a cooling cell at 25°C, 1 Mpa for 1 minute for a brief cooling. During extraction, a number of samples are taken every 10 minutes. Extracts in the form of active compounds in the continuous phase (water) were analyzed for physical and chemical properties and their chemical composition was analyzed using HPLC-MS.

3. Result & Discussion

3.1. Mass transfer solid-liquid

The mechanism of mass transfer in the extraction process of a solution contained in a solid by a liquid until an equilibrium condition is reached takes place in three continuous stages, namely:

1. Solute phase changes occur when the solute changes from the solid phase to the liquid phase. Solutation of solutes occurs through the solid-liquid interface. This phenomenon is considered to occur quickly and does not affect the overall extraction rate

2. The solute diffuses into the solvents found in the pores of the solid. The process of moving solutes from inside solid particles to the surface takes place because of the concentration gradient between the solid-liquid interface and the external surface of the solid. Solvents in the pores remain stationary, therefore the process of moving the solute from the zone with greater
concentration to the outside will occur through a molecular diffusion process. The mass transfer rate of this stage is expressed in equation 1:

\[
N_{AS} = -D_e \cdot A \cdot \frac{dC}{dr}
\]  

with

\[
N_{AS} = \text{mass flux (kg. s}^{-1})
\]

\[
D_e = \text{solute diffusivity (m}^2\text{s}^{-1})
\]

\[
A = \text{diffusion contact surface area (m}^2)
\]

\[
C = \text{solute concentration in solution (kg.m}^{-3})
\]

\[
r = \text{distance of mass transfer (m)}
\]

3. When the solute reaches the particle surface, the solute moves into the solution because there is a concentration gradient. The rate of mass transfer in the solution phase is expressed in equation 2:

\[
N_{AS} = K_{La} V (C_s - C) = \frac{dM}{dt}
\]

With:

\[
M = \text{mass of the solute being moved (kg)}
\]

\[
V = \text{solvent volume (m}^3)
\]

\[
t = \text{time (s)}
\]

\[
C_s = \text{solute concentration on a solid surface, which is equal to solute concentration in a saturated solution (kg.m}^{-3})
\]

\[
K_{La} = \text{volumetric mass transfer coefficient (s}^{-1})
\]

3.2. Ginger Bioactive Hydrothermal Extraction Mass Transfer Model

The hydrothermal extraction events of gingerol, shogaol, ginger paradol are considered as a series of mass transfer events which include:

1. Diffusion of gingerol, shogaol, paradol from the solid to the surface of the solid.
2. Gingerol, shogaol, paradol mass transfer from the surface of the solid to the liquid solvent in the pores of the solid.
3. Diffusion of gingerol, shogaol, paradol in liquid solvents.

The volumetric mass transfer rate of gingerol, shogaol, paradol from the surface of the solid to liquid, where CS is the concentration of gingerol, shogaol, paradol on the surface of the solid which is in balance with the concentration of the solute in the saturated solution. Equation (2) can also be expressed in the form of:

\[
N_{AS} = K_{La} V (C^* - C)
\]  

The correlation between solute concentration in a saturated solution and initial solute concentration in solid solute content in the remaining sample at an infinite time and the mass of the initial sample (m) can be stated in the equation:

\[
m. (C^0 - C^\infty) = VC^*
\]  

\[
\frac{m. (C^0 - C^\infty)}{V} = C^*
\]  

Gingerol mass balance, shogaol, total paradol in solution are expressed in the following equation

\[
N_{AS} = \frac{d(VC)}{dt}
\]

The total differentials of equation are:

\[
N_{AS} = C \frac{d(V)}{dt} + V \frac{d(C)}{dt}
\]
Since there is no change in the volume of the solvent, equation (6) can be simplified to:

\[ N_{AS} = V \frac{d(C)}{dt} \]  

Equation (7) and equation (4.b) are substituted into equation (3) to obtain:

\[ V \frac{d(C)}{dt} = K_{La} V \left( \frac{m(C^0 - C^\infty)}{V} - C \right) \]  

Equation (8) can be rearranged into:

\[ \frac{d(C)}{dt} + K_{La} C = K_{La} \left( \frac{m(C^0 - C^\infty)}{V} \right) \]  

If, \( A = K_{La} \) and \( B = K_{La} \left( \frac{m(C^0 - C^\infty)}{V} \right) \)

Then equation (9) can be changed to:

\[ \frac{dC}{dt} + AC = B \]  

Equation (22) is an ordinal differential equation of order 1. Analytical settlement with the boundary conditions when \( t = 0, C = 0 \) and when \( t = t, C = C \) is obtained:

\[ C = \frac{B}{A} - \frac{B}{A} e^{(-At)} \]  

The \( K_{La} \) value can be obtained through one variable optimization with the help of the Golden Section optimization method or MATLAB calculation software. Optimization is done to obtain the sum square of errors (SSE) or the sum of the squares of the difference between the \( C \) count (\( C_{hit} \)) with the smallest \( C \) experiment (\( C_{perc} \)).

\[ SSE = \sum (C_{hit} - C_{perc})^2 \]  

3.3. Shogaol mass transfer to the subcritical water phase

The mass transfer model in the hydrothermal extraction of ginger shogaol was also verified with experimental data. Figure 2 shows that the hydrothermal extraction rate at the beginning of extraction is very fast. However, after the extraction time of more than 10 minutes, no increase in the extract was obtained. The proposed model matches the experimental data with constants \( A \) and \( B \) found are 3.6912 and 54,078. As shown in Figure 24, the straight line represents the proposed model and most of the data is attached to the line. The mass transfer coefficient (\( K_{La} \)) in the hydrothermal extraction mass transfer model of the Goga shogaol is 3.6912 s\(^{-1}\). The use of green solvents in subcritical areas for the shogaol extraction process will be effective if it is at high temperatures. That is because, at high temperatures, the viscosity and surface tension of the water will decrease so that it will encourage the rate of mass transfer, absorption into the matrix particles and selectivity to [33] [34].

![Figure 2. Profile of shogaol mass transfer to the subcritical water phase](image-url)
4. Conclusion

Hydrothermal extraction using subcritical water can increase the content of shogaol compounds, compared to conventional extraction processes such as soxhletation, percolation, supercritical fluid extraction, microwave extraction, and ultrasonic extraction. The mass transfer coefficient (K_{la}) in the shogaol mass transfer model using subcritical water were 3,750.3 s^{-1}, 3,691.2 s^{-1}, 0.314 s^{-1}, respectively.

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