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Kinetic Modelling of Liquid-Solid Extraction of Bioactive Compounds from Ginger Waste using Subcritical Water

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Abstract

Kinetic modelling played a key role in developing subcritical water extraction for bioactive compounds such as shogaol and gingerol from ginger waste. Liquid-solid extraction kinetics could predict the extraction phenomenon and increase the efficacy of the extraction process. This study aimed to develop a mathematical model of leaching kinetics and determine the extraction rate constant (k) of shogaol and gingerol in the ginger pulp, which is in the subcritical water phase. The research was carried out in two work stages: modelling and experimentation. The modelling compared three extraction kinetic models, namely pseudo-first order, pseudo-second order, and the distribution coefficient. The model was postulated and validated with experimental data using Matlab. The subcritical water extraction of shogaol and gingerol in ginger waste occurred at 140°C with a pressure of 3.5 bar. The extracts were separated from the raffinate and further analysed using HPLC-MS. The results showed that the pseudo-first-order kinetic model described well the subcritical water extraction phenomenon with regression values of 0.9882 for gingerol and 0.9682 for shogaol, respectively. The extraction rate constant (k) of gingerol and shogaol was 0.1101 minute^{-1} *and 0.3130 minute*$^{-1}$*, respectively. This showed that the shogaol extraction rate was higher than the gingerol extraction rate.*

Keywords : *subcritical water, gingerol, extraction kinetic model, shogaol*

INTRODUCTION

Ginger (*Zingiber officinale*) is well-known as a biomass with bioactive compounds such as anticancer (Abdullah et al., 2010; Harliansyah et al., 2007), antioxidants (Harliansyah et al., 2007), and anticarcinogenic (Yusof et al., 2008). The bioactive compounds that show health benefits are gingerol, shogaol, and paradol. Bioactive compounds such as 6-gingerol, 10-gingerol, and 6-shogaol. 6-gingerol is the most abundant compound in the ginger rhizome and provides a positive response in mediating heart contractions as an antioxidant (Antipenko et al., 1999). Therefore, various attempts to extract 6-gingerol and 6-shogoal have been carried out, including prospective extraction using subcritical water (Antipenko et al., 1999; Yulianto et al., 2017;2022).

The extraction of bioactive compounds using subcritical water is typically a green solvent technology. Recently, researchers have been interested in using subcritical water in the extraction method. The solvents in the subcritical region (100-374°C) can increase the ionization constant due to the increase in temperature. In addition, high temperature above 120°C can cause the weakening of hydrogen bonds resulting in large amounts of subcritical water ionization products. Subcritical water can also be a catalyst (Paramita et al., 2019). It is caused by weakened hydrogen bonds resulting in the auto-ionization of water into hydronium ion acid catalysts (H_3O^+) and hydroxide ion base catalysts (OH^-). Furthermore, subcritical water can indirectly reduce the activation energy in the extraction process (Peterson et al., 2008). The subcritical water in the extraction mechanism can reduce viscosity and surface tension, increase the rate of mass transfer, and increase the diffusion rate to 10 times

(Yulianto et al., 2018a,b).

Mass transfer is an important aspect of increasing the extraction rate of gingerol and shogaol from ginger waste and evaluating the performance of subcritical water extractors. Moreover, developing a kinetic model for the solid-liquid extraction (leaching) of shogaol and gingerol compounds can predict the extraction phenomenon. Currently, the physical mass transfer data available in the literature is for 6-gingerol. However, 6-shogaol in subcritical water extraction are very limited. The mass transfer model applied to the extraction of 6-gingerol and 6-shogaol is represented by finding the value of the overall mass transfer coefficient (k); in this case, the value of k represents the extraction rate.

In general, the extraction kinetics of bioactive compounds in ginger waste consists of releasing 6-gingerol and 6-shogaol from a porous or cellular matrix into the solvent through a mass transfer mechanism. 6-gingerol and 6-shogaol, bound to the solid particle matrix of ginger pulp both physically and chemically, are transferred to the solvent phase using the dissolution mechanism (Oliveira et al., 2019). The mass transfer of bioactive compounds to ginger pulp generally has three steps (Hobbi et al., 2021): (i) the solvent mixes with the ginger pulp particles, penetrates the particles, and dissolves the bioactive compounds (solvent penetration), (ii) the dissolved bioactive compounds diffuse to the surface of the particles (internal diffusion), and (iii) bioactive compounds move from the particle surface to the main part of the solution diffusion (external diffusion). The extraction rate constant (k) is calculated based on the solute concentration each time at certain intervals.

Previous research discussed gingerol and shogaol extraction kinetics in ginger waste with hot water at 150°C. The results showed that the extraction rate constant (k) was $6.80 \times 10^{-3}/\text{min}$ for gingerol and $10.90 \times 10^{-3}/\text{min}$ for shogaol (Yusof et al., 2008), respectively. Other studies reported k values with chloroform and n-hexane solvents of $0.0141/\text{min}$ and $0.001554\ \text{L} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ for gingerol rates (Ho et al., 1999; Sala et al., 2010). However, kinetics data of shogaol and ginger pulp extraction using subcritical water are unavailable. Therefore, this study aimed to develop a mathematical model of extraction kinetics and determine the extraction rate constant (k) of shogaol and gingerol in ginger waste using subcritical water as a solvent.

METHODS

The research method was carried out in two work stages: model development and measurement of experimental data in the laboratory. The models developed include extraction kinetics models, namely pseudo-first order, pseudo-second order, and the distribution coefficient approach. The model compiled was validated by fitting experimental data using Matlab calculations as the programming language.

Apparatus and Materials

The main tool is a subcritical water extractor made of stainless steel, which consists of two main parts: a hydrothermal extractor and a cooling unit connected by a ¼ in. stainless pipe. The main ingredient, ginger measuring 5-8 cm, was bought from UMKM Tiga Dara Ungaran. Distilled water, nitrogen, and materials for analysis were purchased at CV. Jurus Maju Semarang.

Methods

Emprit ginger was cleaned from dirt and fed in a grated-squeezing machine to get the ginger pulp. Then, the dried ginger pulp was ground using the 50-mesh sieve. A hundred gram of ginger pulp powder and 4000 ml of distilled water were fed into a stainless tube with a lid as an extraction cell. The cell was closed with a stainless lid, and N_2 gas was introduced into the cell for 2 minutes to remove air and dissolved oxygen. The excess pressure was reduced through the valve. The temperature was set at 140°C by heating the extractor. The extraction process starts (t = 0) when the temperature reached under certain conditions. All experiments were carried out at a pressure of 3.5 bar. After the process was complete, the extract was transferred to a cooling cell at 25°C, 1 MPa for 1 minute to allow brief cooling. During the extraction, several samples were taken every 5 minutes. Extracts of gingerols and shogaols in the continuous phase (water) were analysed for their chemical composition using HPLC-MS. The schematic apparatus of extraction can be seen in Figure 1.

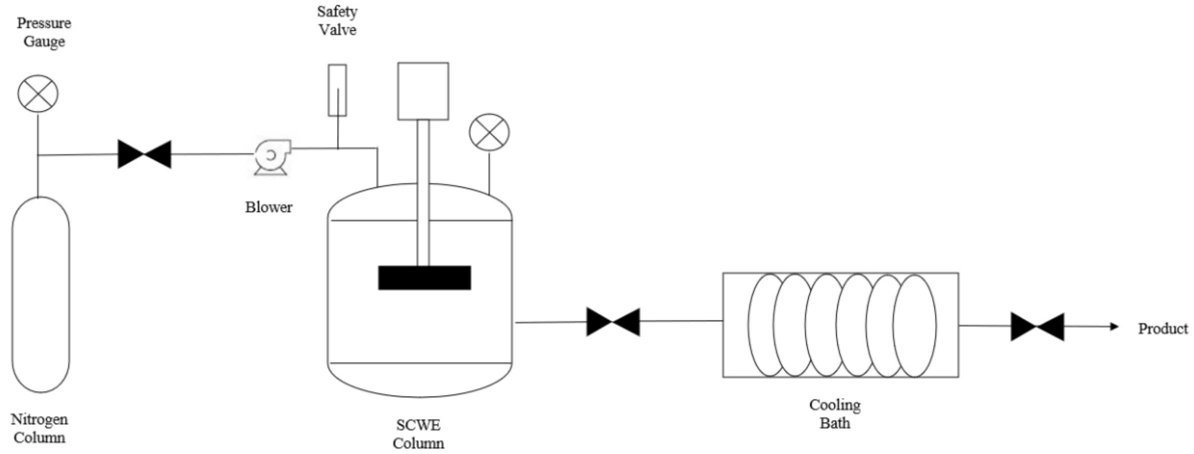

Figure 1. Design of a Subwater Critical Extractor (SCWE)

Kinetic Model Development

The development of the kinetic model in this study compared the three extraction kinetic models to determine the most appropriate phenomenon in describing the mechanism. The assumption that can be made in the extraction mechanism is to ignore the diffusion of compounds due to the relatively small ginger dreg particles, so the extraction mechanism influences this stage. The extraction mechanism to reach the equilibrium state is considered fast, so the appropriate equilibrium model in describing the kinetic model is a pseudo-state type.

Referring to the mechanism, the pseudo-first order kinetic and second order kinetic are taken, which are felt to be able to describe the mechanism. Mass balance was based on the model with Henry's equation approach to describe the equilibrium mechanism in the reaction stages.

Pseudo-first-order kinetics was proposed by Lagergren (Sala et al., 2010). This model illustrates that the rate of extraction kinetics is directly affected by the compound concentration. The general equation for the pseudo-first-order kinetic is proposed according to equation (1).

$$r_e = \frac{dq_t}{dt} = k_1(q_s - q_t) \tag{1}$$

Equation (1) can be solved by determining the boundary conditions at t=0; q_t=0 and, when t=t; q_t=q_t, so the above equation becomes a linear equation like Equation (2)

$$\ln\left[\frac{q_s}{q_s - q_t}\right] = k_1.t \tag{2}$$

Ho (1999) proposed pseudo-second-order kinetic using Equation (3).

$$r_e = \frac{dq_t}{dt} = k_2(q_s - q_t)^2 \tag{3}$$

By integrating the boundary conditions of t=0; q_t=0 and when t=t; q_t=q_t, the final equation obtained is like Equation (4) – (6).

$$\frac{1}{q_s - q_t} - \frac{1}{q_s} = k_2.t \tag{4}$$

$$\frac{t}{q_t} = \frac{t}{q_s} + \frac{1}{q_s^2 k_2} \tag{5}$$

$$\frac{t}{q_t} = \frac{t}{q_s} + \frac{1}{y} \tag{6}$$

The equations show that k_1 (minute^{-1}) and k_2 (g/mg.minute) are the extraction rate constants to reach an equilibrium level in the pseudo-first order and pseudo-second order, where q_s is the amount of solute extracted in an equilibrium state (mg/gram), q_t is the amount of solute extracted at time t (mg/g), and t is the extraction time (minute).

Moreover, the basis of the mass balance was compared, and an approach was made with the distribution coefficient equation arranged according to Equations 7-11. The assumption showed that the ginger pulp particles were small so the diffusion of bioactive components in the ginger pulp was considered fast and ignored.

Mass balance of bioactive components in fluids

Mass inflow - outgoing mass rate = Accumulated mass rate

$$k_a.a.m(C_a^* - C_a) - 0 = \frac{d}{dt}(V.C_a) \tag{7}$$

$$\frac{dC_a}{dt} = \frac{-k_a.a.m}{V}(C_a - C_a^*) \tag{8}$$

Mass balance of bioactive components in solids

Mass inflow - outgoing mass rate = Accumulated mass rate

$$-k_a.a.(C_a^* - C_a)\,m - 0 = \frac{d}{dt}(m\,X_a) \tag{9}$$

$$\frac{dX_a}{dt} = k_a.a.(C_a - C_a^*) \tag{10}$$

The following equation cannot be solved with certainty because there is a notation from C_a^*, which is specifically incalculable. Thus, the equation approach to solve C_a^* is to use the distribution coefficient equation.

$$X_a = K_d.C_a^* \tag{11}$$

Equations 7-11 can be translated from the notation as follows, k_a is the speed of bioactive extraction (m/min^{-1}), m is the mass of ginger pulp used (grams), V is the volume of solution (litres), Ca* is the bioactive concentration in the liquid phase at equilibrium (mol/litre), Ca is the bioactive concentration in the liquid, $\frac{dC_a}{dt}$ is the distribution of bioactive concentrations in the liquid every time (mol/minute), $\frac{dX_a}{dt}$ is the bioactive concentration in the ginger pulp each time (mol/minute), K_d is a constant equilibrium value, and a is the surface area of the ginger pulp (m^2). The measurable variables in this study can be seen in Table 1.

Table1. Variables for calculations.

Variable	Unit	Value
Mass (m)	gram	100
Volume (V)	Litre	4
Surface area for ginger dregs (a)	m^2	1

RESULT AND DISCUSSION

Results of Extraction of Bioactive Compounds on Ginger Dregs

Figure 2 presents the extraction yield curve of gingerol and shogaol compounds as a function of time. The gingerol and shogaol concentrations increased with the extraction time. This happens because the longer the extraction time, the longer the chance of contact between the solute phase and the solvent phase so that more solute crosses over to the solvent phase. The study results show that the gingerol curve has a different slope; this is due to differences in the mechanism of mass transfer on the surface of the ginger pulp. Gingerol gain after 10 minutes tends to be constant, leading to an equilibrium state (Romdhane et al., 2005). Furthermore, the yield of 6-shogaol 0.00056 mol/minute for the 20th minute at 140°C was greater than that of 6-gingerol of 0.0001853 mol/minute. Therefore, further studies need to determine the extraction rate constant using the physical data of extraction kinetics.

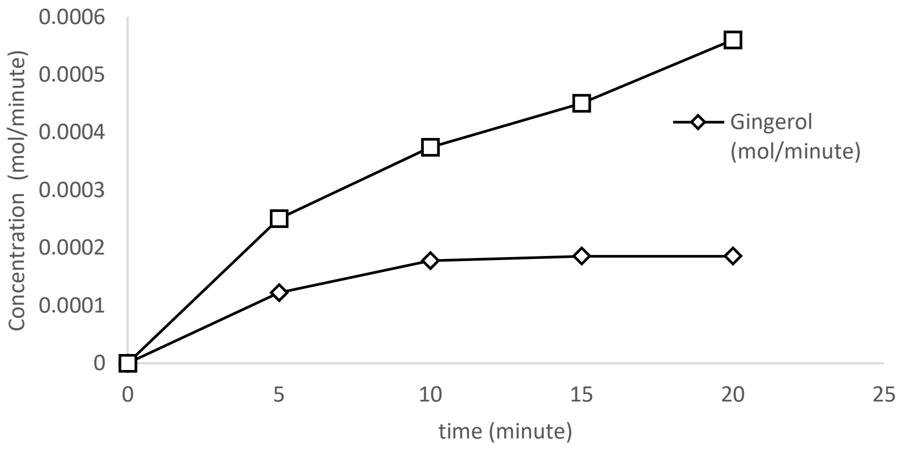

Figure 2. Extraction of bioactive compounds from ginger dregs

Kinetic of Bioactive Compounds Extraction of Ginger Dregs

The kinetics of ginger pulp bioactive compounds extraction is presented in Figure 3-5. Extraction data was used in determining the kinetic rate of extraction of ginger dregs in the range of 5 minutes to 20 minutes. The kinetics of extraction model were developed based on pseudo-first order, pseudo-second order, and coefficient distribution approaches.

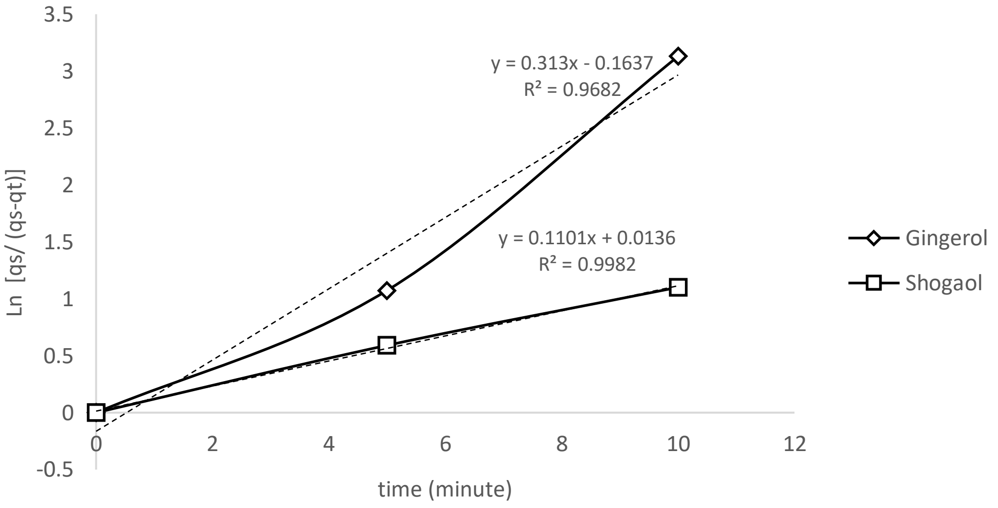

Figure 3. Pseudo-First Order Bioactive Extraction Kinetics

Figure 2 presents the plotting of the data used to find the value of the extraction velocity constant (k). The x-axis shows the extraction time (minutes), and the y-axis is ln [Cs/(Cs-Ct)]. Based on the graph plotting, the resulting slope represents the value of k. The gingerol extraction rate constant was 0.1101/minute, while the shogaol extraction rate constantt was 0.313/minute. These results indicate that the extraction rate of shogaol is much faster than gingerol because some of the gingerols are hydrated to become shogaol. This is in accordance with the statement that at a temperature of 140°C and a microwave power of 1000 W, gingerol is dehydrated into shogaol with the help of microwaves combined with sour food seasonings (Guo et al., 2015).

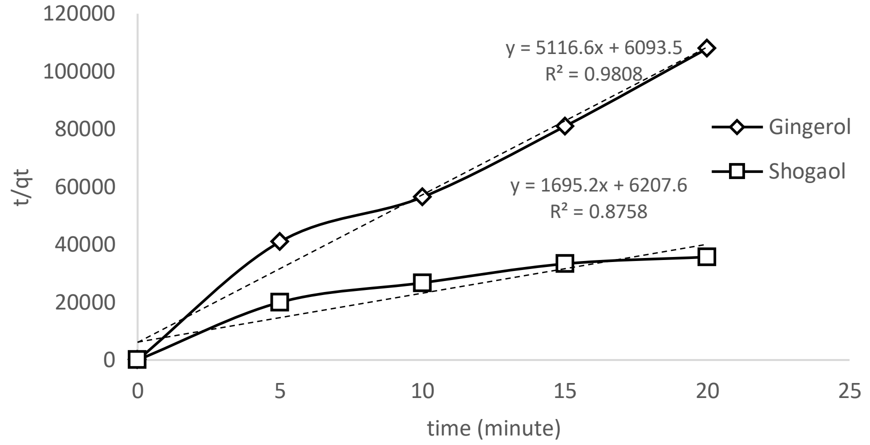

Figure 4. Pseudo-Second Order bioactive extraction kinetics

The constant value of the extraction speed with the pseudo-second-order model is presented in Figure 3. Correlation between time (minutes) is on the x-axis and t/Ct on the y-axis. The determination of extraction speed constant is calculated based on the intercept value obtained. The gingerol extraction rate constant was 6.2686 x 10^{-12} g/(mg.minute), while shogaol extraction rate constant was 6.000 x 10^{-11} g/(mg.minute). This means that the extraction rate of shogaol is faster than gingerol for the pseudo-second-order kinetic model.

Figure 4 presents the results of the fitting between research data and calculations to determine the value of the extraction rate constant using the distribution coefficient approach model. The gingerol extraction rate constant was 0.0106 m/min, and shogaol extraction rate constant was 0.0118 m/min, meaning that the gingerol extraction rate was much lower than that of shogaol. Meanwhile, the equilibrium constant (K) value for gingerol and shogaol was 1.0089 and 0.9693, respectively. The value of the extraction equilibrium constant is the ratio of the solute in the solvent to the solute in the solid whose value is close to one, meaning that the solute increases moving to the solvent phase.

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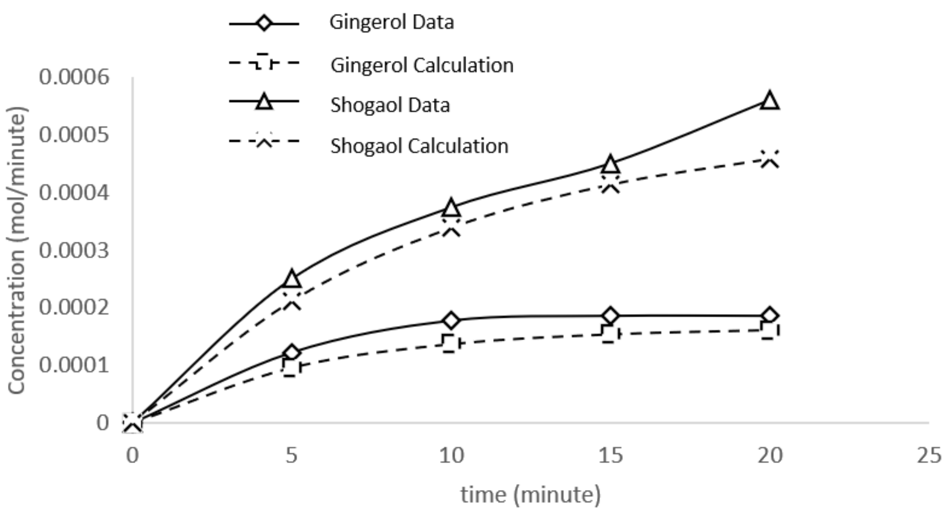

Figure 5. The kinetics of bioactive extraction based on the distribution coefficient

Constant data for the development of the pseudo-first order, pseudo-second order, and the distribution coefficient approach in detail are presented in Table 1. The coefficient of determination R^2 in the pseudo-first-order kinetic model is relatively the largest, which means the model can illustrate the extraction mechanism. Other studies showed the trend of the same results, where the rate constant of extraction rate for shogaol is greater than for gingerol. Kinetic study with operating conditions of 150°C found that the k value for gingerol was 6.80 x 10^{-3}/minute and shogaol 10.90 10^{-3}/minute using a pseudo-first-order kinetic model. In addition, the proposed model modification in the distribution coefficient (k) value for gingerol was 2.75 x 10^{-7} m/s and 4.40 x 10^{-7} m/s for shogaol (Sarip et al., 2014).

Table 2 presents the extraction rate constant values for various references. The study results showed that the extraction rate constant using subcritical water was greater than the reference k value. This happens because subcritical water has a higher solubility as temperature increases, causing a decrease in the value of the dielectric constant of water (Eikani et al., 2007). The use of subcritical water can reduce the viscosity and surface tension so that it will increase the rate of mass transfer, absorption into the matrix particles, and selectivity (Teo et al., 2010; Sarip et al., 2014; Yulianto et al., 2017;2018a,b) and increase the diffusivity up to 10 times (Yulianto et al., 2017;2018a,b). Therefore, the subcritical water solvent in the extraction of ginger pulp bioactive compounds is very prospective to be developed.

Table 1. Comparison of pseudo-first models, pseudo-second models, and distribution coefficients

Model	k	Kd	R^2
First-order kinetic model			
Gingerol	0.1101/minute		0.9882
Shogaol	0.3130/minute		0.9682
Second-order kinetic model			
Gingerol	6.2686 x 10^{-12} g/mg.minute		0.8758
Shogaol	6.0000 x 10^{-11} g/mg.minute		0.9808
Distribution coefficient			
Gingerol	0.0106 (m/ minute)	1.0089	0.7462
Shogaol	0.0118 (m/ minute)	0.9693	0.9192

Table 2. Comparison of k values with other studies

Extraction Method	Operating Conditions	K Value	Reference
Hot compressed water	150°C 3.5 MPa	Gingerol: 6.80 10^{-3}/minute Shogaol: 10.90 10^{-3}/minute	(Oumarou et al., 2007)
Chloroform Solvent	30°C 450 rpm	Gingerol: 0.0141/minute	(Sarip et al., 2014)
N-Hexane Solvent	50°C - 60°C	Gingerol: 0.001554L/(gram. minute)	(Shadmani et al., 2004)

CONCLUSION

Kinetic model for extracting shogaol and gingerol from ginger dregs can be developed using subcritical water pseudo-first order, pseudo-second order, and coefficient distribution approaches. The pseudo-first-order kinetic model can describe the phenomenon of subcritical water extraction, with the acquisition of regression values of 0.9882 for gingerol and 0.9682 for shogaol, respectively. Extraction speed constant values (k) obtained were 0.1101/minute for gingerol and 0.3130/minute for shogaol.

REFERENCES

Abdullah, S., Abidin, S.A.Z., Murad, N.A., Makpol, S., Ngah, W.Z.W., Yusof, Y.A.M. (2010). Ginger extract (Zingiber officinale) triggers apoptosis and G0/G1 cells arrest in HCT 116 and HT 29 colon cancer cell lines, *Afr. J. Biochem. Res.* 4, 134–142.

Antipenko, A.Y., Spielman, A.I., Kirchberger, M.A. (1999). Interactions of 6-gingerol and ellagic acid with the cardiac sarcoplasmic reticulum Ca21-ATPase1, *J.Pharmacol. Exp. Ther.* 290, 227–234.

Eikani, M.H., Golmohammad, F., Mirza, M., Rowshanzamir S. (2007). Extraction of volatile oil from cumin (Cuminum Cyminum L.) with superheated water, *J. Food Process Eng*. 30: 255–266.

Guo, J.B., Zhang, W.J., Wu, H., Du, L.M. (2015). Microwave-assisted decomposition coupled with acidic food condiment as an efficient technology for ginger (Zingiber officinale Roscoe) processing. *Separation and Purification Technology*, 146, 219–226.

Harliansyah, Murad, N.A., Ngah, W.Z.W., Yusof, Y.A.M. (2007). Antiproliferative, antioxidant and apoptosis effects of Zingiber officinale and 6-gingerol on hepG2 cells, *Asian J. Biochem*. 2, 421–426.

Ho, Y.S., McKay. G. (1999). Pseudo second order model for sorption processes. *Proc Biochem*. 34, 451-465.

Hobbi, P., Okoro, O,V. Delporte, C., Alimoradi, H., Podstawczyk, D., Nie, L., Bernaerts, K.V., Shavandi, A. (2021). Kinetic Modelling of thr solid-liquid extraction process od polyphenol compounds from apple pomace: influence of solvent composition and temperature, *Bioresources and Bioprocessing*. 8, 1-12.

Oliveira, E.R., Carvalho, G.R., Cirillo, M.A., Queiroz, F.Q. (2019). Effect of Ecofriendly BioBased Solvent on Oil Extraction from Green Coffee Bean and its Industrial Press Cake, *Brazilian Journal of Cemical Engineering*. 36.

Oumarou, H.A.H., Fauduet, H., Porte, C., Ho, Y.S. (2007). Comparison of Kinetic Models for the Aqueous Solid-Liquid Extraction of Tilia Sapwood in a Continuous Stirred Tank Reactor, *Chemical Engineering Communications*. 195, 537-552.

Paramita, V., Yulianti, M.E., Hartati, I., Bahrudin, U., Broto, R.T.D.W. (2019) Optimization on subctitical fluid extraction of Zingiberene, *Journal of Vocational Studies on Applied Research*. 1, 18-21.

Peterson, A.A., Vogel, F., Lachance, R.P., Froling, M., Antal, M.J., Tester, J.W. (2008). Thermochemical biofuel production in hydrothermal media: A Review of sub-and supercritical water technologies, *Energy Environ*. Sci. 1, 32-65.

Romdhane, M., Tizaoui, C. (2005). The kinetic modelling of a steam distillation unit for the extraction of aniseed (Pimpinella anisum) essential oil, *Journal of Chemical Technology & Biotechnology*. 80, 759-766.

Sala, L., González, J. (2010). Thermodynamic and dynamic of chromium biosorption by pectic and lignocellulocic biowastes, *Journal of Water Resource and Protection*, Vol.2 No.10.

Sarip, M.S.Md., Morad, N.A., Ali, M.A.M., Yusof. Y.A.M., Yunus, M.A.C. (2014). The kinetic of extraction of the medicinal ginger bioactive compounds using hot compressed water, *Separation and Purification Tech*. 124, 141-147.

Shadmani, A., Azhar, I., Mazhar, F., Hassan, M.H., Ahmed, S.W., Ahmad, I., Usmangjanis, K., Shamim, S. (2004). Kinetic Studies od Zingiber Officinale, *Pakistan Journal of Pharmaceutical Sciences*. 17, 47-54.

Wang, Y., Wang, C., Xue, H., Jin, Y., Yang, M., & Leng, F. (2022). Comparative analysis of three kinds of extraction kinetic models of crude polysaccharides from codonopsis pilosula and evaluate the characteristics of crude polysaccharides. *Biomass Conversion and Biorefinery*, 1-17.

Yulianto, M.E., Kusumo, P., Hartati, I. (2017). Subcritical water extraction of gingerol from Zingiber officinale. *Rasayan Journal of Chemistry*. 10 (1): 738-743.

Yulianto, M.E., Paramita, V., Hartati, I., Amalia, R. (2018a). Response Surface Methodology of Pressurized Liquid Water Extraction of Curcumim from *Curcuma domestica val*, *Journal of Chemistry*. 11, 1564-1571.

Yulianto, M.E., Paramita, V., Hartati, I., Handayani, D. (2018b). Hot Compreesed Water Extraction of Curcumin from *Curcuma domestica val*, AIP Conference Proceedings. 1977, 1130-1143.

Yulianto, M.E., Purwantisari, S., Hartati, I., Nisa, Q.A.K., Nyamiati, R.D. (2022) Subcritical reactive extraction of shogaol and gingerol: effect of time and temperature, *International Food Research Journal*. 29, 857-863.

Yusof, Y., Ahmad, N., Das, S., Sulaiman, S., Murad, N. (2008). Chemopreventive efficacy of ginger (Zingiber officinale) in ethionine induced rat hepatocarcinogenesis, *Afr. J.Tradit. Complement. Altern. Med*. 26, 87–93.