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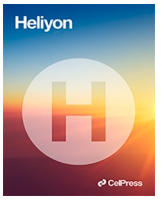

Research article

Kinetic parameter for scale-up and γ-oryzanol content of rice bran oil as antioxidant: Comparison of maceration, ultrasonication, pneumatic press extraction

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ABSTRACT

Rice bran oil is one of oryzanol source oils. Oryzanol is an antioxidant compound that is related to the absorption of cholesterol, and is used in hyperlipidemia treatment and menopause problems. RBO extraction, purification and its γ-oryzanol content have been carefully reviewed. The quality and concentration of γ-oryzanol depend on the extraction process and purification. In selecting the extraction method to obtain the highest oryzanol content, in addition to comparing the concentration of oryzanol obtained and it can also be done by comparing the extraction kinetics parameters. Modeling according to physical or empirical kinetics can contribute in increasing the result of extraction. This study aims to determine the highest oryzanol content in rice bran oil, comparing several extraction methods and studies of rice bran oil extraction kinetic is necessary for scale up purposes. In this study is conducted Rice Bran Oil Extraction with n-Hexane solvent using several different methods, such as maceration, ultrasonication, and pneumatic press extractions. Independent variable that is used is the extraction time and yield as dependent variable. The study shows that the best extraction method to get the highest yield is 10.34 % by ultrasonicator and oryzanol content is 5.09 mg/g by a pneumatic press machine. According to kinetic parameter k_2 is 0.001546, Cs is 0.0589, and h is 0.4707, $R^2 = 0.9715$ obtained from extraction using ultrasonicator.

1. Introduction

Based on the study by Ref. [1] Rice bran oil (RBO) is one of oryzanol source oil. Oryzanol is an antioxidant compound that is related to the absorption of cholesterol, and otherwise used in hyperlipidemia treatment and menopause problems. RBO extraction and purifi-cation and its γ-oryzanol content have been carefully reviewed. The quality and concen-tration of γ-oryzanol depend on the extraction process and purification. The sample ex-tracted using hexane contains high content of γ-oryzanol. According to Ref. [2], rice

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bran oil is highly nutritious and contains unsaturated fatty acid and antioxidants like oryzanol, to-copherol, tocotrienol, phytosterol, polyphenol, and squalene. Ferulic Acid (FA) is a part of phenol fraction with the highest yield of 24 % at 80 % ethanol concentration and Ultra-sonication extraction method. Both Oryzanol and Ferulic acid are antioxidant and an-ti-inflammatory contained in rice bran oil [3]. states that the γ-oryzanol extracted from rice bran oil is commonly used for beauty products, including face cream, skin care. Cream products that are rich is antioxidant claim to offer better protection from the UV light, pollution, and heat.

A study conducted by Ref. [4] states that the comparison of extraction methods to obtain high bioactive content of phenolic compounds from the propolis, by doing double mac-eration method, double microwave treatment and double ultrasound extraction using 70 % ethanol. Ultrasonic extraction has higher extraction result compared to microwaves and maceration extractions, 271.65 mg/g propolis [5]. states that γ-oryzanol from rice bran can be extracted using n-Hexane solvent and isopropanol (1:3) with ultrasonic bath extraction method with centrifugation time variation. Quantitative test result of γ-oryzanol sample with 25 min centrifugation time contains the highest ɣ-Oryzanol level of 2.84 mg/g. This result shows that the longer the centrifugation time is allocated, the higher content of ɣ-Oryzanol is obtained. In choosing the extraction method to get the best content of oryzanol, aside from comparing the oryzanol level parameter, kinetic study parameter comparison can also be used as [6] did in their study, which states that modeling based on physical or empirical kinetics and by optimizing model parameter may contribute in increasing the extraction result. This research studied the effect of various extraction processes on oil extraction, oxidative stability, bioactive compounds, and antioxidant activity of crude rice bran oil. The extraction processes used are extraction with hexane solvent, cold pressing extraction, cold pressing extraction with thermal pretreatment, and cold pressing extraction with ultrasonic pretreatment. The results showed that thermal cooking and ultrasonic pretreatment increased the oil extraction yield in the cold pressing extraction process [7].

Temperature and solvent/rice bran ratio influence the oil extraction yield. The experimental data follows a kinetic model for solid-liquid mass transfer. Thermodynamic studies show that both solvents are endothermic, spontaneous and irreversible processes. Ethyl acetate solvent achieves higher extraction yields at the start and highest yields in a shorter time due to better compatibility with the oil in rice bran and low viscosity [8]. Base on [6] Empirical and/or semi-empirical model, mathematical description for extract effi-ciency variation or operation parameter result are used a lot due to its quick and eco-nomical use in various types of processing. Mathematical modeling can provide useful information to increase extraction system and/or process and help researchers and de-signers to obtain the most effective process condition and great design parameter for op-timization purposes. Various mathematical models, such as first-order, second-order, Weibull, and Peleg kinetical models are used to illustrate the result of active ingredient's ultrasonication. Thus, to obtain the best content of oryzanol in rice bran oil, comparing different extraction methods and study of kinetic parameter of rice bran oil extraction is necessary for scale-up purposes.

2. Materials and methods

2.1. Material and equipment

The materials used in this study consist of rice bran from Central Java, Indonesia, N-hexane 98–99 % Technical Grade (Sari Kimia), and distilled water. The equipment for this experiment consists of ultrasonicator bath Merk Wisd WiseClean, beaker, stirrer, frying pan, oven, and rotary evaporator R-100, Merk: Buchi.

2.2. Procedure

This study conducted Rice Bran Oil Extraction with n-Hexane solvent using several different methods, such as maceration, ultrasonication, and pneumatic press extractions. Independent variable used in this study is ultrasonication extraction time and dependent variable is yield.

2.3. Extraction with maceration method

By adding n-hexane with ratio of 1: 7 (v/v) [9], maceration method was used for the extraction. This process continues by pouring a hexane solvent into a beaker along with the rice bran. After maceration, the extract obtained was separated to take the filtrate and continued with the separation of rice bran oil and solvent using a rotary evaporator. The results were analyzed for the yield using spectrophotometry to ensure the γ-oryzanol content in rice bran oil was at the highest yield and its antioxidant properties.

2.4. Extraction with ultrasonication method [10]

N-hexane solvent was added 7 times the volume of rice bran, ultrasonication method is used to carry out extraction treatment with the ultrasonic time as independent variable, varying from 5, 10, 15, 20, 25 min. This process continues by pouring a hexane solvent into a beaker along with the rice bran. Following the ultrasonication, The extract obtained is filtered from the cake using filter paper, then the rice bran oil is separated from the solvent using a rotary evaporator for 10–15 min. The results were analyzed for the yield using spectrophotometry to ensure the γ-oryzanol content in rice bran oil was at the highest yield and its antioxidant properties.

2.5. Extraction with pneumatic press method [11]

The extraction with pneumatic press requires 200 g of rice bran, 10-min stabilization, and 7-bar pressure and the addition of solvent

with a volume ratio to rice bran seven times, Pneumatic Press method is used to carry out the extraction treatment by preparing a furring cloth in a pneumatic press. Rice bran that has been macerated with hexane for 3 h is poured into a pneumatic press. After being processed by pneumatic press, the filtrate taken after the extraction results was filtered in an Erlenmeyer. A rotary evaporator is used to recover the solvent by separating it from the rice bran oil for 10–15 min. The results from rotary evaporator were analyzed for the yield using spectrophotometry to ensure the γ-oryzanol content in rice bran oil was at the highest yield and its antioxidant properties.

2.6. Analysis of rice bran oil extract yield

According to Ref. [12], rice bran oil is yield is calculated by using equation (1)

$$Yield = \frac{A}{B}\, x\, 100\% \tag{1}$$

Where.

A = Mass of extracted
B = Mass of raw material

And according to Ref. [13], from the result of sandalwood oil extraction experiment, the following equation found the yield of sandalwood oil (2)

$$Yield = \frac{v}{w}\, x\, 100\% \tag{2}$$

Where:
Sandalwood oil yield is represented by Y (%, w/w), weight or mass of extracted sandal oil (g) is represented by V and weight or mass of sandalwood powder (g) is represented by W.

2.7. Analysis of oryzanol content in rice bran oil [5]

Determining γ-Oryzanol content with High Performance Liquid Chromatography (HPLC) Method. HLPC System used for γ-Oryzanol compound with Acetonitrile mobile phase: Butanol: Asetic acid: Aquadest (94:3:2:1), immobile phase C18, waters detector 2996 PDA (Photodiode Array Detector), waters symmetry column 5 μm wave length UV detector 320 nm. Each sample weighs 1.62 g. -γ-Oryzanol standard with concentration of 500 ppm is weighed at 2.5 mg. 2 ml of sample is solved with solvent in 5 ml volumetric flask, filtered, and poured into the vial, and then injected with HPLC. HPLC test result is obtained as peak area from chromatogram graphics, and from that area the γ-Oryzanol content on the sample can be calculated.

2.8. Analysis kinetic of extraction

A study by Ref. [14] seeks for the most suitable kinetic model to explain about extraction of vanillic acid from pumpkin seed. Root mean square (RMS), standard deviation, and correlation coefficient were used to test the experimental kinetic data model. Physical models (unsteady state diffusion model, film theory model) and empirical models (hyperbolic model, second order model, Elovich model, and Ponomarev model) are used to test the extraction kinetics. Extraction kinetic parameters were used to evaluate the extraction potential of vanillic acid from pumpkin seeds. The unsteady state diffusion model is expressed in Eq. (3) and can be restructured as linear equation. (4) :

$$\frac{q}{q0} = (1-b)e^{-kt} \tag{3}$$

$$ln\ \frac{q}{q0} = \ln(1-b) - kt \tag{4}$$

Where; the level of vanillic acid in the liquid extract during the extraction is represented by q (mg/g), q_0 is the initial level of vanillic acid in the pumpkin seeds (mg/g), k represents the slow extraction coefficient of the unsteady-state diffusion model (1/min), b represents the washing coefficient of the unsteady-state diffusion model.

According to Ref. [14], if R^2 is higher than RMS value and SD is lower, the suitability will be better. Determining best kinetics is conducted with comparing the value of k. Data processing is conducted by comparing the biggest result of each method. Stated by Ref. [13], first-order and second-order diffusion model and the linearization results are as follows:

Sandalwood oil extraction kinetic using microwave hydro-distillation extraction is determined by comparing the value of R^2 between the first-order and second-order equation. First-order model extraction The pseudo first-order equation of Lagergen can be rewritten in its differential form as follows:

$$\frac{dC_t}{dt} = k_1(C_s - C_t) \tag{5}$$

Where, k_1 represents the first-order extraction rate, constant (min^{-1}), and t (min) represents time. Equation (2) was integrated with application of the boundary conditions Ct = 0 at t = 0 and Ct = Ct at t = t.

$$\ln\left(\frac{c_s}{c_s - c_t}\right) = k_1 t \tag{6}$$

Rearrangement of equation (6) is possible to obtain the linear form:

$$\log(C_s - C_t) = \log(C_s) - \frac{k_1}{2.303} t \tag{7}$$

Present researchers analyzed the plots of log(C_S - Ct) against t for varying operating conditions is used to calculate the constant k1 of the slope and the equilibrium extraction capacity C_S (concentration obtained at the saturation point) from the intercept. The following is the second-order kinetic equation for the extraction rate

$$\frac{dC_t}{dt} = k_2(C_s - C_t)^2 \tag{8}$$

Where, k_2 represents the rate constant of the second-order extraction (L g^{-1} min^{-1}), C_S represents the extraction capacity (essential oil concentration at saturation in g L^{-1}) and Ct represents the sandalwood oil concentration at any time t (min). By considering the initial and boundary conditions, t = 0 to t and Ct = 0 to Ct, the integrated rate law for a second-order extraction was obtained:

$$C_t = \frac{C_S^2 k_2 t}{1 + C_S k_2 t} \tag{9}$$

By transforming Eq. (8), a linear form shown in Eq. (9) can be achieved and the extraction rate is seen in Eq. (10):

$$\frac{t}{C_t} = \frac{1}{k_2 C_S^2} + \frac{t}{C_S} \tag{10}$$

$$\frac{C_t}{t} = \frac{1}{\left(1/k_2 C_S^2\right) + \left(t/C_S\right)} \tag{11}$$

The initial extraction rate, h, as Ct/t when t approaches 0, can be defined as

$$h = k_2 C_S^2 \tag{12}$$

and, the essential oil concentration at any time can be expressed after rearrangement as,

$$C_t = \frac{t}{(1/h) + (t/C_S)} \tag{13}$$

Experimentally, to determine the initial extraction rate (h), the extraction capacity (C_S) and the second-order extraction rate constant (k) from the slope and intercept, one can plot t/Ct versus t [15]. The value of first-order and second-order is compared to each other based on the slope and the intercept of plot, k, C_S, and the coefficient of determination, R^2.

2.9. Determining extraction method for the highest γ-oryzanol extraction

From the highest yield extraction, γ-oryzanol content, and extraction kinetic (k), the best extraction method with the best result can be determined.

3. Results and discussion

3.1. Maceration extraction and kinetic study

Extraction of rice bran with n-hexane solvent with ratio 1:7 (v/v) is conducted with maceration time of 1 day, 2 days, 3 days, 4 days,

Table 1
RBO yield resulted from Maceration extraction with n-hexane solvent of the ratio of 1: 7 (v/v) and maceration time (day) independent variable.

Maceration Time, day, t	RBO Concentration, Ct g/L	dCt/dt (from equation 5	log (Cs-Ct) (from equation 7	t/Ct ((from equation (10))
0	0	0	0.866878	–
1	5.28	5.3	0.318063	0.189
2	5.81	2.9	0.190332	0.688
3	6.34	2.1	0.0086	1420
4	7.22	1.8	−0.85387	2.216
5	7.36	1.5	–	3.397
STDEV	2.73	1.76	0.62	1.27

5 days as independent variable with yield as dependent variable. Extraction result with maceration time as the independent variable can be seen in Table 1. Based on extraction time and yield data in Table 1, data processing is conducted to obtain extraction kinetic analysis result, by referring to the study by Ref. [13] using the approach and assumption following the pseudo first-order equation and second-order equation. Yield data is used as oil concentration/extract data. Study result data can be seen in Table 1.

Based on Table 1, a curve that illustrates the relationship between Ct vs t and dCt/dt vs Ct is made, as equation (5)) and resulted in the curve in Figs. 1 and 2.

Based on Fig. 2 and By following the linear equation (8): Slope $k_1 = 0.8716$; Intercept k_1 Cs = 5.3299; Cs = $5.3299/k_1 = 6.1150$; $R^2 = 0.8045$. Next we find the value of k by using equation (8).

Based on Fig. 3 and by following the linear equation (7)): Slope: $0.3751 = -k_1/2.303$, $k_1 = 0.8638$, Intercept Log Cs = 1.2313, then the value of Cs = 17.0333; $R^2 = 0.9008$. Next we find the value of k by using equation (7). Then if mass transfer kinetics is studied using second-order kinetic model approach by using equations (8) and (9) and has been processed in Table 1 and curve can be seen in Fig. 4.

Based on Fig. 4 and by using equation (10)), slope is 1/Cs = 0.7944; so the value of Cs = 1.26 and the value of k_2 obtained by intercept is $0.8012 = k_2\ Cs^2$, so the value of $k_2 = 0.50$ From equation (12)) in the beginning of extraction t = 0, so the value of h = 0.8012. Meanwhile the value of $R^2 = 0{,}9766$. Mass transfer kinetic study in the maceration extraction follows the second-order model with the respective constant value of k = 0.5, Cs = 1.26, h = 0.8012with $R^2 = 0.9766$.

3.2. Ultrasonication extraction

Extraction of rice bran with n-hexane extraction with the ratio of 1:7 (v/v) is conducted with ultrasonication time of 5 min, 10 min, 15 min, 20 min, 25 min independent variable with yield as dependent variable. Extraction result with ultrasonication time as independent variable can be seen in Table 2.

Based on Table 2, a curve illustrating the relationship between Ct vs t and log (Cs-Ct) vs t was made, just as equation (5)) and the curve is illustrated in Figs. 5 and 6.

Based on Fig. 6 and by following the linear equation (7)): Slope: $0.2482 = -k_1/2.303$, $k_1 = 0.5716$ Intercept log Cs = 1.1733, then the value of Cs = 14.9039; $R^2 = 0.9452$. Then if mass transfer kinetics is studied using second-order kinetic model approach by using equations (8) and (9) and has been processed in Table 2 then curve can be seen in Fig. 7.

Based on Fig. 7 and by using equation (9)), slope is 1/Cs = 0.4707; so the value of Cs = 0.0589 and the value of k_2 obtained from the intercept is $0/2662 = k_2\ Cs^2$, so the value of $k_2 = 0.001546$. From equation (11)) in the beginning of extraction, t = 0, so the value of h = 0.4707; value of $R^2 = 0.9715$. The second-order model mass transfer kinetic study in the ultrasonication extraction with the respective constant value of k = 0.001546, Cs = 0.0589; h = 0.4707 with $R^2 = 0.9715$.

3.3. Pneumatic press extraction

The weight of each sample is 200 gr with stabilization time varying from 8, 11, 14, 17 and 20 min for the extraction process using pneumatic press machine with constant pressure of 7 bar as seen in Table 3.

Based on Table 3, curve was created to illustrate the relationship between Ct vs t and dCt/dt vs Ct, as in equation (5)) and the results are in Figs. 8 and 9.

Based on Table 3 and Fig. 8, namely the relationship between Ct and stabilization time, t at the pneumatic press extraction, the highest concentration value was carried out at a stabilization time of 14 min, 7.035 %. When compared with [16] roasting at 80C and 3 min, the yield is 0.17 (g/g) and the oryzanol content is 9.10 mg/g.

Based on Fig. 9 and By following the linear equation (5), obtained slope $k_1 = 1.5189$; Intercept k_1 Cs = 5.2613; Cs = $5.2613/k_1 = 3.4639$; $R^2 = 0.6425$. Then if mass transfer kinetics is studied using second-order kinetic model approach by using equations (8) and (9) and has been processed in Table 3 and curve can be seen in Fig. 10.

Based on Fig. 10 and by using equation (9)), slope is 1/Cs = 0.3967; so the value of Cs = 2.52 and the value of k_2 is obtained from the intercept that is $1.0331 = k_2\ Cs^2$, so the value of $k_2 = 0.16$ and from equation (11)) in the beginning of extraction t = 0, so the value

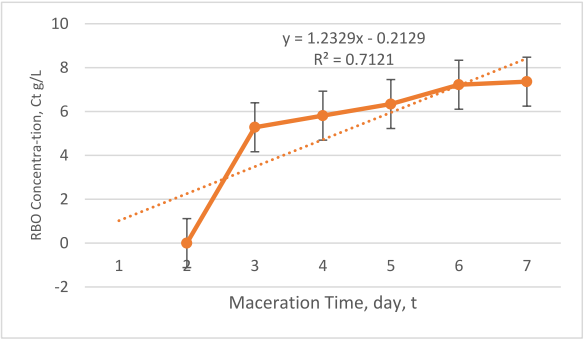

Fig. 1. The relationship among time, day and Oil Concentration Ct (g/L) from maceration extraction.

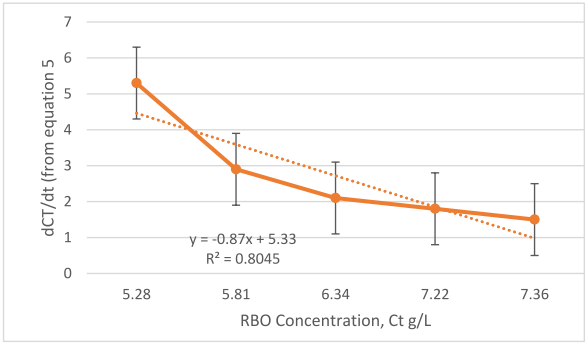

Fig. 2. The relationship between dCt/dt vs Ct from the result of maceration extraction.

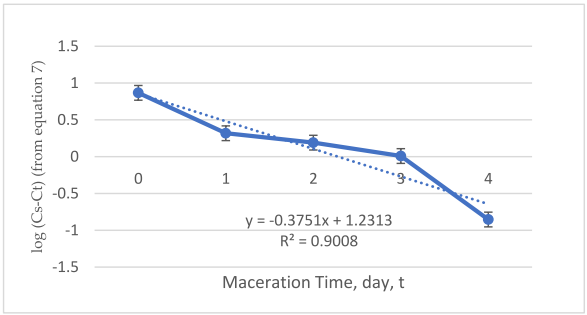

Fig. 3. Curve illustrating the relationship between Log (Cs-Ct) vs t.

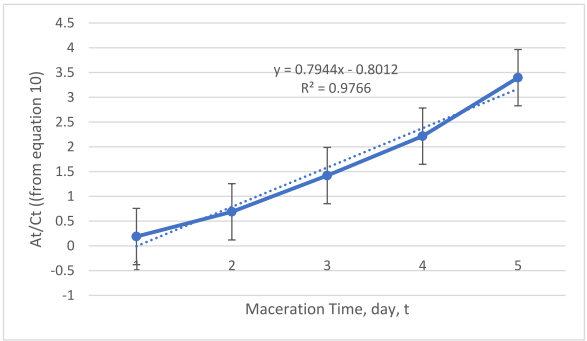

Fig. 4. Curve illustrating the relationship between t/Ct vs t.

Table 2
RBO yield, result of Ultrasonication extraction with n-hexane solvent on the ratio of 1: 7 (v/v) and ultrasonication time (minute) as independent variables.

Ultrasonication Time, Minute, t	% RBO Yield, concentration, Ct	log (Cs-Ct) (from equation 7	t/Ct (from equation (9))
0	0	1.014521	0
5	6.58	0.575188	0.75987842
10	7.84	0.39794	1.2755102
15	8.42	0.283301	1.78147268
20	9.74	−0.22185	2.05338809
25	10.34	−0.22185	2.41779497
STDEV	3.75	0.48	0.89

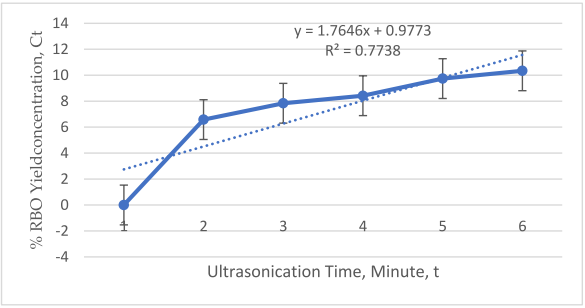

Fig. 5. Curve illustrating the relationship among t, day, and Oil Concentration, Ct (g/L) from Ultrasonication extraction.

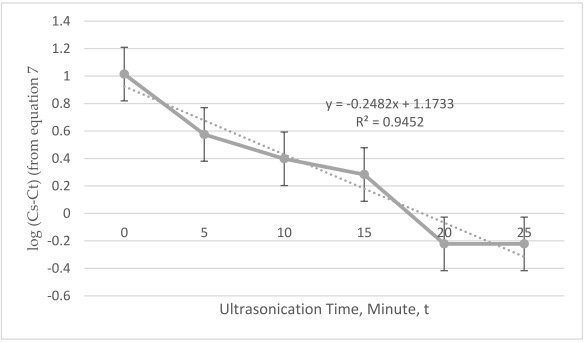

Fig. 6. Curve illustrating the relationship between Log (Cs-Ct) vs t from Ultrasonication extraction.

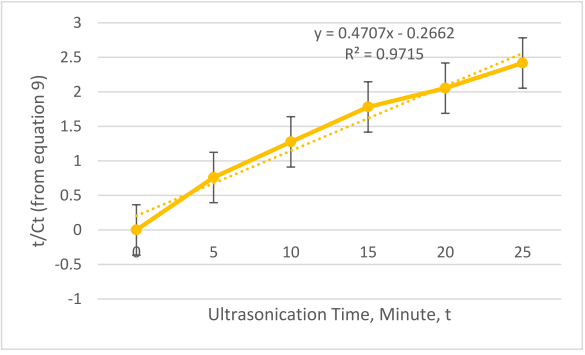

Fig. 7. Curve illustrating the relationship between t/Ct vs t from equation (9).

Table 3
Stabilization Time Variation Data and RBO yield (%) in the extraction process using pneumatic press machine with constant pressure of 7 bar.

Stabilization Time in the extraction with pneumatic press (Minute)	% RBO yield (concentration), Ct	dCT/dt (from equation (5))	t/Ct ((from equation (9))
8	4.71	0	1.6985
11	6.7	5.13	1.6418
14	7035	0.3875	1.9900
17	6.63	0.2133	2.5641
20	6.21	0,125	3.2206
STDEV	0.91	2.47	0.67

of h = 1.0331 and the value of $R^2 = 0.8845$. Mass transfer kinetic study in the pneumatic press extraction is the second-order model with respective constant values of $k_2 = 0.16$, Cs = 2.52, h = 1.0331 with $R^2 = 0.8845$, k_2 is the second-order extraction rate constant (L g-1 min-1), Cs the extraction capacity (concentration of essential oil at saturation in g L-1) and Ct is the concentration of sandalwood

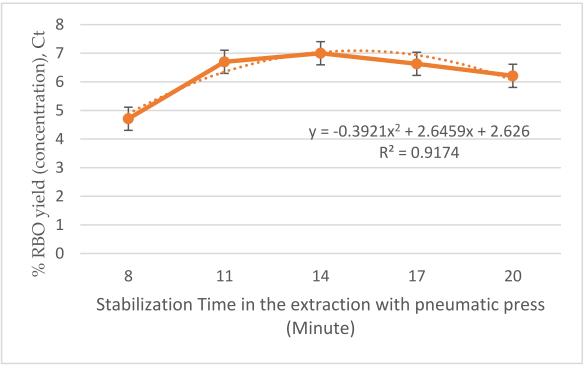

Fig. 8. The relationship among stabilization time, t, minutes and Oil Concentration, Ct (g/L) from the pneumatic press extraction.

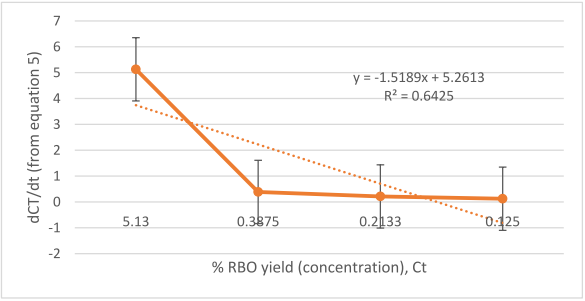

Fig. 9. The relationship between dCt/dt vs Ct from equation (5) with the pneumatic press extraction.

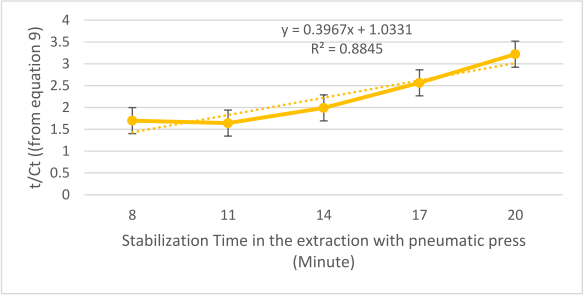

Fig. 10. The relationship between t/Ct vs stabilization t of pneumatic press extraction result from equation (9).

oil at any time t (min). The initial extraction rate, h, the extraction capacity, CS, and the second-order extraction rate constant, k. When compared with [13] sandalwood oil extraction using the microwave-assisted hydrodistillation method, the value of $k_2 = 0.0343$, Cs = 0.6797, h = 0.0158, $R^2 = 0.9961$, these results indicate that these two methods give the same results, that the extraction kinetics model is second-order.

The first order model based on diffusion phenomenon into solid is represented by equation (5)) and [17].

$$q(t) = q_\infty \left[1 - e^{-t/T}\right] = q_\infty \left[1 - e^{-kt}\right] \tag{14}$$

Where q(t) is the essential oil yield at extraction time t,

Q∞ is the asymptotic yield at infinite time and.

T is the time constant.

The term 1/T = k is the kinetic constant including the effective diffusion coefficient.

The pseudo-second-order kinetic using Equation (8)) and [18].

$$re = \frac{dqt}{dt} = \widehat{k}2\ (qs - qt)\hat{2} \tag{15}$$

Where t = 0; qt = 0 and when t = t; qt = qt,

The differences in the kinetic parameters are caused by (i) the dependence on consentration: firs-order model linearly on the consentration whereas second order model depend on the square of the consentratio; (ii) The rate constant units (k) also differ. First-order model, the unit of k is typically minute^{-1} (time $^{-1}$), while for second –order model, it is M − 1 min-1 (per mol/mass per time)

The effectiveness of the oil release from the rice bran is influenced by several parameters throughout the extraction process. According to Ref. [19], (i) Cell Wall Disruption: The rice bran's cell walls are physically damaged by the extraction techniques used, which makes it easier for oil to escape. For instance, ultrasonication produces imploding cavitation bubbles that send shock waves into the cell walls, breaking them [20]. Beside that, (ii) Solvent Penetration: Effective oil extraction depends on the solvent's ability to penetrate the rice bran efficiently. The oil is dissolved by the study's use of solvents such n-hexane, enabling its separation from the solid [21]. The yield and oryzanol content are highly dependent on the extraction technique and solvent selection; (iii) Temperature and Pressure Effect; Variations in temperature and pressure, particularly when using the press extraction method, can change the oil's viscosity and facilitate its extraction. These circumstances may also impact the oil's solubility of γ-oryzanol, which could result in increased levels of this antioxidant in the extracted oil; (iv) Solvent-Oil Interaction; An essential aspect of extraction is the interaction between the solvent and the constituents of the oil. Solvent properties such as polarity, boiling point, and compatibility with oil influence the extraction efficiency [22,23] and the quality of the oil obtained, including its γ-oryzanol content. Also, (v) Oryzanol Solubility: the solubilization of γ-oryzanol and other bioactive compounds in the solvent might be affected by the process conditions. The amount of γ-oryzanol extracted depends on several factors, including the extraction time, solvent-to-material ratio, and specific extraction processes (maceration, ultrasonication, pneumatic press).

The underlying principles of solubility and diffusion essentially control how much oil is released into the solvent during the extraction process. This procedure can be broken down into multiple parts, which are frequently determined by the extraction technique (such as solvent extraction, mechanical pressing, or ultrasonic-assisted extraction). A condensed description is provided below [24]. First, Contact and Penetration: The substance containing the oil—in this case, rice bran—comes into touch with the solvent. For solvent extraction, the solvent penetrates the solid, reaching the oil cells. In methods like ultrasonication, the process is accelerated by cavitation effects [20], which enhance solvent penetration through the cellular matrix. Second, Solubilization: The oil dissolves into the solvent after it has entered the cells. An important consideration in this case is the oil's solubility in the solvent. The choice of solvent is determined by how well it can dissolve the oil; n-hexane, for instance, is frequently employed due to its superior oil-solving capabilities. The oil-solvent mixture diffuses out of the cell upon solubilization. Third, The concentration gradient in the solvent between the outside environment (lower oil concentration) and the interior of the cell (high oil concentration) drives this diffusion process. Fourth, The solvent now containing the dissolved oil is then separated from the solid matrix. Both centrifugation and filtration can be used to accomplish this. Ultimately, Fifth: the extracted oil is left behind after the solvent is eliminated from the oil-solvent mixture, usually by evaporation or distillation.

The chemical properties of the solvent affects its ability to dissolve the oil; higher temperatures can increase solvent penetration and oil solubility; pressure can improve the contact between the solvent and the oil; smaller particle sizes of the solid matrix increase the surface area for solvent contact, facilitating better extraction efficiency; and agitation technique are some of the factors that can affect the efficiency of oil release into the solvent, according to Ref. [24]. To obtain the optimum extraction efficiency and the highest potential oil content from rice bran, each of these parameters must be tuned. The ultrasonic extraction method yielded the maximum yield in this study.

Based on the data processing in the kinetic parameter study of rice bran oil extraction with maceration, ultrasonication, and pneumatic press methods, the data obtained are illustrated in Table 4.

Based on Table 4, the highest value of the second-order chemical mass transfer coefficient with a pneumatic press is 2.52, the value of $R^2 = 0.8845$. The R^2 value is the high, which indicates how much influence certain independent variables have on the dependent variable. If compared to other extraction methods is lowest and higher than order 1 modeling for pneumatic press. These results are similar to research [13] on sandalwood extraction using microwave-assisted hydro distillation. According to Ref. [25] Kinetics evaluation via the Peleg model showed that solvent extraction reached steady state after 15 min whereas ultrasound assisted extraction reached steady state after only 1 min and produced very similar results for rice bran oil and γ-orizanol. The result of research from Ref. [26] show that The second order kinetic parameters of the gamma oryzanol extraction model from dried rice bran soapstock show that the values of Cs, k and h increase with increasing ultrasonic power (from 0.5 W/g to 4.5 W/g) and extraction temperature (from 35 °C to 45 °C). Cs and h decreased when the extraction temperature increased from 45 °C to 55 °C.

Using the data in Table 5, an ANOVA test was carried out to determine the significance of 2 factors, namely time and mass transfer order for 3 extraction methods, namely maceration, ultrasonication and pneumatic press. The F test results show the values as shown in

Table 4
Kinetic parameter of rice bran oil extraction with maceration, ultrasonication, and pneumatic press methods.

	Maceration		Ultrasonication		Pneumatic Press	
	First-order	Second-order	First-order	Second-order	First-order	Second-order
Cs	6.1150	1.26	14.9039	0.0589	3.4639	2.52
k_1	0.8716	–	0.5716	–	1.5189	–
k_2	–	0.5	–	0.001546	–	0.16
h	–	0.8012	–	0.4707	–	1.0331
R^2	0.8045	0,9766	0.9452	0.9715	0.6425	0.8845

Table 5. Meanwhile, based on the analysis of mass transfer kinetics, it is known that in the three extraction methods the mass transfer is order 2 considering that the R^2 value of order 2 is higher than order.

On the data in Table 5, an ANOVA test was carried out to determine the significance (0.05) of the model with 2 factors, namely time and reaction order for 3 extraction methods, namely maceration, ultrasonication and pneumatic press. The results of the F test show the values as shown in Table 5, namely the maceration method shows that it is not significant (F count (0.900145) < F table (7.708647). Meanwhile, the Ultrasonication Method shows significant (F count (11.128426) > F table (7.708647)) and the method The Pneumatic Press shows a significant (F count (26.14441) > F table (4.45897)) indicating that based on the analysis of mass transfer kinetics, it is known that in the three extraction methods the mass transfer is order 2 considering that the R^2 value of order 2 is higher than order 1.

3.4. γ-oryzanol characterization in RBO

γ-oryzanol characterization in RBO with maceration, ultrasonication, and pneumatic press methods in the highest yield can be seen in Table 6.

Comparative studies of γ-Oryzanol content in RBO using Maceration, Pneumatic Press, and Ultrasonication methods from Table 6 shows the highest value of oryzanol content in extraction using a pneumatic press machine which is 5.09 mg/g higher than the results of research [27] using multistage extraction with hexane and ethanol solvents, obtained 0.9 mg/g.

The differences Cs values (extraction capacity or saturation concentration) observed in first and second –order kinetics, as well as between different extraction methods, can be attributed to several factors: (i) Kinetic order: first-order: the rate is directly proportional to the concentration (eq (5))). The Cs value in the first order reflect the saturation consentration on the extraction and Cs is obtained from the intercept of the line equation; second order: the extraction rate is proportional to the square of the concentration (eq. (8)) [13]. The Cs value indicates the maximum concentration of product. In extraction processes, it presents the maximum amount of solute (e.g., oil, γ-oryzanol) that can be extract in the solvent; (ii) Differences between Extraction Methods: The extraction method significantly influences the Cs value, because it affects the efficiency and mechanism of solute release the matrix into the solvent. Factors include the method's ability to discrupt cell walls, solute –solvent interaction, and mass transfer efficiency [19,20], and [21]. Maceration: involves soaking the solid matrix in solvent, relying passive diffusion to extract the solute. This method may lead to lower Cs value due to limited solvent penetration and slow diffusion rates; Ultrasonication: uses ultrasound waves to create cavitation, disrupting cell structures and enhancing solvent penetration. This can result in higher Cs values because of the more efficient extraction of solutes; Pneumatic press: Applies physical pressure to squeeze the solute out of the matrix. The effectiveness and Cs values can vary based on the pressure applied and how well the solute is released from the matrix; (iii) Physicochemical Properties of the Solute and Solvent: The intrinsic solubility of the solute in the solvent and the solvent's ability to penetrate the solid matrix are crucial. Higher solubility and better penetration typically result in higher Cs values; Conditions that improve solubility and diffusion generally increase Cs; (iv) Matrix Characteristics: The composition of the matrix (e.g., rice bran) and particle sice of the solid affect the extraction efficiency. Smaller particles and matrices typically lead to higher Cs.

The observed differences in Cs values across first and second-order kinetisc and between extraction methods stem from the kinetic's nature, the efficiency of each method, and the physicochemical interaction between solute, solvent, and matrix.

The ultrasonication is the best method for extraction rice bran oil dan maximizing the yield of γ -oryzanol, an antioxidant compound beneficial for health. The ultrasonication considered superior, based on the kinetic parameters and γ -oryzanol content: (i) Efficiency in Yield and Oryzanol Content: Ultrasonication achieved the highest yield of 10.34 % among the methods tested, with oryzanol content of 4.08 mg/g, which is significant compared tomaceration and pneumatic press methods. This high efficiency is pivotal for scale-up purposes and industrial application where maximizing yield and active compound content is crucial; (ii) Kinetic Parameters: The ultrasonication method showed favorable kinetic parameters with a second-order model. Specifically, is demonstrated a kinetic parameter k_2 of 0.001546, Cs of 0.0589, and h of 0.4707, with a high correlation coefficient ($R^2 = 0.9715$). Indicating that the ultrasonication process is well-described by the model and thus can be effectively scaled up based on the parameters; (iii) Rapid and Effective Extraction: Ultrasonication facilitates the extraction process by introducing high-frequency sound waves that create microbubbles in the solvent, geretares localized high temperatures and pressures, improving the mass transfer between the solid and liquid phases. This mechanism enhances the penetration of solvent into the rice bran matrix; (iv) Optimization and Scale-Up Potential: The kinetic study and the empirical modelling of the ultrasonication process provide valuable insight into optimizaing the extraction condition for maximum yield and oryzanol content. The detailed analysis of kinetic parameters allow for precise scaling up the process, making ultrasonication a viable and economically feasible option for industrial application; (v) Energy Efficiency and Process Intensification: It requires less solvent and energy, making it environmentally friendly and cost-effective choise; (vi) Quality extract: The ultrasonication method not only yileds a higher percentage of RBO and oryzanol but also ensures the preservation of the oil's

Table 5
ANOVA results with F test analysis using Two Factor ANOVA without replication.

Extraction Methode	ANOVA Test	
	F	F crit
Maceration	0.900145	7.708647
Ultrasonication	11.12843	7.708647
Press Penumatic	26.14441	4.45897

Table 6
γ-Oryzanol content on several extraction methods with the highest yield.

Extraction methods on the highest yield	Oryzanol mg/g
5 days maceration	3.88
25 min ultrasonic	4.08
6 bars press	5.09

nutrition and functional properties.

4. Conclusions

The yield and concentration of γ-oryzanol are influenced by the extraction and purification process methods. The highest oryzanol content can be obtained by comparing the extraction method and mass transfer kinetic parameters in the extraction process. The research results showed that the best extraction method to obtain the highest yield was using an ultrasonicator, namely 10.34 % with an oryzanol content of 4.08 mg/g. Comparison of extraction methods based on kinetic parameters shows that the best values are k_2: 0.001546, Cs: 0.0589, and h: 0.4707 at $R^2 = 0.9715$ which were obtained from extraction using an ultrasonicator. It's necessary for scale-up purposes. Ultrasonication stands out as the most effective method for extracting RBO and maximizing γ-oryzanol content due to its efficiency, favorable kinetic parameters, and potential for optimization and scale-up, offering a promising avenue for industrial application in producing high-quality rice bran oil rich in antioxidants.

Data availability

Data associated with this study been deposited into a publicly.

CRediT authorship contribution statement

Ratri Ariatmi Nugrahani: Writing – review & editing. **Tri Yuni Hendrawati:** Methodology. **Ummul Habibah Hasyim:** Data curation. **Fatma Sari:** Formal analysis. **Anwar Ilmar Ramadhan:** Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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