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Research article

Optimization and kinetics of ultrasound-assisted solvent extraction of gamma oryzanol from dried rice bran soapstock

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Abstract

The effect was investigated of ultrasound-assisted solvent extraction (UASE) parameters on gamma oryzanol recovery from dried rice bran soapstock (DRBS) using a mixture of ethyl acetate and ethanol. The UASE parameters were ultrasound power (0.5 W/g, 2.5 W/g, 4.5 W/g), extraction temperature (35°C, 45°C, 55°C) and sonication time (4 min, 15 min, 26 min). The study used ethyl acetate:ethanol ratios (volume per volume; v/v) of 100:0%, 95:5%, 90:10%, 85:15%, 80:20% and 75:25% and the optimal ethyl acetate:ethanol mixture was 85:15% v/v. In the study, the UASE parameters were first optimized using a response surface method (RSM)-based, face-centered, composite design for maximum DRBS gamma oryzanol recovery. Subsequently, the kinetic behavior of the UASE process was characterized using a second-order kinetic model based on variable ultrasound power and extraction temperature, for a given sonication interval. The optimal RSM-based UASE condition was 4.0 W/g ultrasound power, 50°C extraction temperature and 21.50 min sonication time, achieving maximum predicted and experimental gamma oryzanol recoveries of 98.03% and 98.15%, respectively, which were in good agreement. The simulated and experimental kinetic results were also in agreement (coefficient of determination > 0.972), validating the applicability of the kinetic model for characterizing the effect of UASE parameters on DRBS gamma oryzanol recovery.

Introduction

Rice bran oil is an excellent source of essential nutrients, including fatty acids, vitamin E (tocopherols and tocotrienols), vitamin K, and gamma oryzanol (Patel and Naik, 2004; Gunstone, 2011). In particular, gamma oryzanol helps to reduce plasma cholesterol (Wilson et al., 2007) and platelet aggregation and cholesterol absorption (Sharma and Rukmini, 1986). Gamma oryzanol is also used in cosmetic products for its anti-itching and anti-dandruff properties (Seetharamaiah and Prabhakar, 1986).

However, crude rice bran oil is high in free fatty acids (FFA) and wax (Gunstone, 2011) and consequently requires chemical refining (degumming, neutralization, bleaching, deodorization) to remove the undesirable compounds. Of particular interest is chemical neutralization where aqueous sodium hydroxide (NaOH) is used to remove FFA by forming a soapstock, thus trapping neutralized rice bran oil and gamma oryzanol. According to Gopala Krishna et al. (2001), nearly 90% of gamma oryzanol was lost through wet soapstock.

Soapstock is mostly converted into toiletry and detergent products (Narayan et al., 2006), feedstock (Ju and Vali, 2005) and lecithin products (Thurman, 1961). In fact, gamma oryzanol in rice bran soapstock has great potential for commercial-scale production

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(Narayan et al., 2006). Specifically, Kumar et al. (2009) extracted gamma oryzanol from dried rice bran soapstock (DRBS) using various solvents (ethyl acetate, ethyl methyl ketone, hexane, acetone, isopropanol) assisted by conventional extraction; and documented that ethyl acetate was ideal for gamma oryzanol extraction (97–99% yield using 6 hr extraction) due to its low polarity and viscosity. Kaewboonnum et al. (2010) experimentally extracted gamma oryzanol from rice bran soapstock using ethyl acetate. Ethanol, a nontoxic and ecological-friendly replacement, has been used to extract vegetable oil and antioxidant compounds (Gunstone, 2011). Nevertheless, there are no known studies on gamma oryzanol extraction from rice bran soapstock using a mixture of ethyl acetate and ethanol. Therefore, the current study explored the possibility of extracting gamma oryzanol from DRBS (assisted by ultrasound) using a mixture of ethyl acetate and ethanol.

Ultrasound-assisted extraction has been increasingly adopted because of its lower process temperatures, shorter extraction time, ease of operation and high efficiency (Gayas and Kaur, 2017). In ultrasound-assisted extraction, mechanical cavitation is induced, resulting in liquid turbulence, accelerated solvent diffusion, cell wall disruption, enhanced mass transfer of target compounds and thus, an improved extraction yield (Vetal et al., 2013). Interestingly, the existing research on gamma oryzanol extraction from rice bran soapstock has focused mainly on conventional solvent extraction (Seetharamaiah and Prabhakar, 1986; Venkatadri and Sreesaila, 2005; Kaewboonnum et al., 2010), with no reported studies focusing on ultrasound-assisted extraction.

Gamma oryzanol extraction efficiency is closely related to the ultrasound-assisted solvent extraction (UASE) parameters which in turn play an important role in the extraction kinetics. Kinetics study helps to determine the factors that affect the extraction process. In this research, a solid-liquid, second-order kinetic model was utilized to characterize the kinetic behavior of the UASE process extracting DRBS gamma oryzanol with a mixture of ethyl acetate and ethanol.

Thus, this research aimed to investigate the effect of UASE parameters, namely ultrasound power (0.5 W/g, 2.5 W/g, 4.5W/g), extraction temperature (35°C, 45°C, 55°C), sonication time (4 min, 15 min, 26 min) on the gamma oryzanol recovery from DRBS using a mixture of ethyl acetate and ethanol at ratios (volume per volume (v/v) of 100:0%, 95:5%, 90:10%, 85:15%, 80:20%, and 75:25%. A response surface method (RSM)-based, face-centered, composite design was used to optimize the extraction parameters for maximum gamma oryzanol recovery. Furthermore, a second-order kinetic model was used to characterize the kinetics of the UASE process under variable ultrasound power and extraction temperature, for a given sonication interval.

Materials and Methods

Materials

Prior to the experiment, rice bran oil wet soapstock was pretreated in 1.25% wt NaOH solution and reacted at 80°C for 15–30 min with constant stirring until the moisture content was 55.0% (Venkatadri and Sreesaila, 2005). The soapstock was then centrifuged and decanted before vacuum evaporation (100°C, 550 mmHg) for 2–3 hr to obtain DRBS with 4.0–4.5% moisture content; this was used as the starting material for extraction.

Methanol (99.9%), *n*-hexane (99.0%) and ethanol (98.5%) were obtained from Sigma-Aldrich (Darmstadt, Germany) and the NaOH anhydrous pellets (98%) came from Carlo Erba reagent (Val-de-Reuil, France).

Experimental methods

Gamma oryzanol extraction using ethyl acetate extraction

Samples (20 g) of DRBS in thimbles were extracted with ethyl acetate at 90°C for 4 hr using a Soxhlet extractor (Kaewboonnum et al., 2010) with a solvent-to-solid ratio of 10:1 (Kumar et al., 2009). The gamma oryzanol rich fraction was then centrifuged at 10,000 revolutions per minute (rpm) and 10°C for 10 min to remove solids; then, the solvent was vacuum-evaporated (55°C, 500 mmHg) to dryness. The resulting gamma oryzanol content was 4.41 ± 0.21 g/100 g DRBS (control 1).

Gamma oryzanol extraction by mixed solvent extraction

Samples (20 g) of DRBS were extracted using a mixture of ethyl acetate and ethanol, where the ethanol concentration was 5%, 10%, 15%, 20% or 25% v/v. The solvent-to-solid ratio was 10:1 (Kumar et al., 2009), and the Soxhlet extraction was carried out at 90°C for 4 hr. The gamma oryzanol rich fraction was then centrifuged and the solvent evaporated. The maximum gamma oryzanol recovery achieved under the optimal ethyl acetate:ethanol ratio was used as control 2.

Ultrasound-assisted solvent extraction

An ultrasonic generator equipped with a titanium-alloy tip probe (25 mm in diameter) with 40 kHz operating frequency (VCX750 Vibracell; Sonic & Materials, Inc., Newtown, CT, USA) was used for the ultrasound-assisted solvent extraction (UASE). In the extraction, 20 g DRBS in a 500 mL flask was mixed with 200 mL ethyl acetate/ethanol mixture at the optimal ethanol concentration from the previous section. The mixtures were ultrasound-treated, using different ultrasound power levels (X_1) of 0.5–4.5 W/g, extraction temperatures (X_2) of 35–55°C and sonication times (X_3) of 4–26 min with a 5 s pulse duration. The gamma oryzanol rich fraction was then centrifuged at 10,000rpm for 10min and vacuum-evaporated (55°C, 500 mmHg) to dryness. The gamma oryzanol recovery was determined in relation to control 2, using Equation 1:

$$\text{Gamma oryzanol recovery (\%)} = \frac{\text{Weight of recovered gamma oryzanol}}{\text{Control 2}} \times 100 \quad (1)$$

Experimental design for gamma oryzanol extraction from dried rice bran soapstock

A face-centered, composite design (FCCD) was used in the implementation of a response surface methodology (RSM) to optimize the extraction parameters using the MODDE software (version 5.0; Umetri, Umeå, Sweden). The extraction parameters (independent variables) were ultrasound power (X_1), extraction temperature (X_2) and sonication time (X_3); each parameter was varied at three levels (low, moderate, high) coded as -1, 0 and +1, respectively (Table 1). The design of the experiment consisted of 17 experimental runs in triplicate; the responses (Y) were averaged.

Table 1 Extraction parameters (independent variables) of face-centered, central composite design

Symbol	Variable	Level		
		-1	0	+1
X_1	Ultrasound power (W/g)	0.5	2.5	4.5
X_2	Extraction temperature (°C)	35	45	55
X_3	Sonication time (min)	4	15	26

A second-order polynomial model was used to predict the gamma oryzanol recovery (Y) as shown in Equation 2:

$$f(Y) = \beta_0 + \sum_{n=1}^{k} \beta_i X_i + \sum_{n=1}^{k} \beta_{ii} X_i^2 + \sum_{i}^{k-1} \sum_{j}^{k} \beta_{ij} X_i X_j \quad (2)$$

where Y is the predicted response; β_0 is a constant; X_1, X_2 and X_3 are independent variables and β_i, β_{ij} and β_{ii} are the linear coefficients, interaction coefficients, and quadratic coefficients, respectively.

The model adequacy was evaluated based on lack of fit (LOF), an F-test and the coefficient of determination (R^2) using analysis of variance (ANOVA). Experiments were carried out and the model was validated by comparing the experimental results against predicted gamma oryzanol yields. The statistical difference was tested at $p < 0.05$.

Kinetic model of ultrasound-assisted solvent extraction

A second-order kinetic model was applied to characterize the kinetic behavior (Lazar et al., 2016). Specifically, the kinetic analysis was performed under two scenarios: (i) variable ultrasound power (0.5 W/g, 2.5 W/g, 4.5 W/g), given 45°C extraction temperature, and (ii) variable extraction temperature (35°C, 45°C, 55°C), given 2.5 W/g ultrasound power. In addition, 85:15 (v/v) ethyl acetate-to-ethanol mixture (the determined optimal mixture ratio) was used as the extraction solvent, while the sonication time was varied between 0 min, 4 min, 8 min, 12 min, 16 min and 21.5 min (the RSM-based optimal sonication time was 21.5min).

According to Lazar et al. (2016), the second-order kinetic extraction model can be expressed using Equation 3:

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \quad (3)$$

where C_t is the concentration of gamma oryzanol (grams per liter) at a given sonication time (t, minutes), k is the second-order extraction rate constant (liters per gram minutes) and C_s is the concentration of gamma oryzanol at saturation (grams per liter).

The kinetic parameters were derived by integrating the second-order kinetic equation under the boundary conditions of $C_t = 0$ - C_t and $t = 0$ - t, and can be written as Equation 4 and in a linearized form using Equation 5:

$$\frac{t}{C_t} = \frac{1}{k.C_s^2} + \frac{t}{C_s} = \frac{1}{h} + \frac{t}{C_s} \quad (4)$$

$$\frac{t}{C_t} = \frac{1}{k.C_s^2} + \frac{t}{C_s} = \frac{1}{h} + \frac{t}{C_s} \quad (5)$$

where h is the initial extraction rate (grams per liter minute) when t and C_t approach 0 and can be defined using Equation 6 (Lazar et al., 2016):

$$h = k.C_s^2 \quad (6)$$

where C_s and k are determined from the slope and intercept, respectively, by plotting t/C_t against t.

Analytical methods

Quantitative analysis of gamma oryzanol content

The gamma oryzanol content was analyzed using UV-spectrophotometry/near infrared spectroscopy (NIR; Shimazu, UV-2600; Kyoto, Japan) following Joshi et al. (2016). Further verification involved subsequently analyzing the gamma oryzanol using high performance *liquid chromatography* (HPLC) according to Sakunpak et al. 92014), with an Agilent 1200 Series HPLC (Agilent Technologies, Inc.; Santa Clara, CA, USA) equipped with a pump (LPG 3X00), auto sampler (ACC-3000), Poroshell 120 EC-C18 column (3.0 mm × 150 mm, 2.7 µm), and diode-array ultraviolet (UV)/visible spectrum detector. The UV detector and the column temperature were operated at 325 nm and 25°C. The mobile phases using 100:0 (v/v), 50:50(v/v) and 40:60 (v/v) methanol-to-acetonitrile were carried out sequentially for 5 min each, with gradient elution at a flow rate of 1.0 mL/min. The injection volume was 20 µL.

Scanning electron microscopy

Scanning electron microscopy (SEM; JEOL, JSM 6010 LV, JEOL Technology Development Ltd.; Tokyo, Japan) was used to characterize the effect of ultrasound on the morphology of DRBS. In the analysis, DRBS and UASE-treated DRBS were placed on a metal stub and gold-sputtered and the most representative SEM images were selected.

Statistical analysis

All analyses were performed in triplicate, with average and standard deviation values computed using Statgraphic centrution

XV (Statsoft Inc.; Liverpool, NY, USA). ANOVA was carried out to determine the effects of the variable extraction parameters on the gamma oryzanol recovery. Tukey's honest significant difference test was used to compare the means at $p < 0.05$.

Results and Discussion

Mixed solvent extraction

The effects of the variable ethyl acetate:ethanol mixtures on DRBS gamma oryzanol recovery using Soxhlet extraction were investigated. Ethanol concentrations in the range 0–15% (v/v) did not significantly affect the DRBS gamma oryzanol recovery (4.39–4.41 g/100 g DRBS). On the other hand, higher ethanol concentrations (20-25% v/v) significantly lowered the gamma oryzanol recovery (4.05 g/100 g DRBS), which could be attributed to the high polarity and viscosity of ethanol. Specifically, a high solvent viscosity hinders mass transfer, thus lowering the gamma oryzanol extraction efficiency (Kumar et al., 2009). In addition, lower gamma oryzanol yields could be attributed to the reduced solubility of gamma oryzanol in alcohol (Narayan et al., 2006).

Thus, a 15% ethanol concentration (85:15% v/v) was adopted to optimize the UASE condition for extracting DRBS gamma oryzanol. In addition, ethanol is less costly and more environmental-friendly than ethyl acetate.

Regression analysis of gamma oryzanol extraction

In this study, RSM-based FCCD was used to optimize the UASE parameters—ultrasound power (X_1), extraction temperature (X_2) and sonication time (X_3)—to maximize the DRBS gamma oryzanol recovery. The interactions between extraction parameters and gamma oryzanol recovery were also evaluated. Table 2 tabulates the experimental and predicted DRBS gamma oryzanol recovery values, which were in the range 73.21–96.71%.

The ANOVA results (Table 3) of the fitted quadratic model for gamma oryzanol recovery indicated that the model terms were significant. In addition, non-significant difference between the model and the experimental data suggested a satisfactory fit.

The robustness and predictive ability of the model were evaluated based on the coefficient of determination (R^2), the adjusted R^2 and model predictive ability (Q^2). The high R^2 (0.983) and adjusted R^2 (0.961) values indicated good agreement between the experimental and predicted data. Q^2 was 0.933, indicating that high predictive ability of the model. In addition, the difference between the adjusted R^2 and Q^2 values was less than 0.30, suggesting the validity of the model (Veerasamy et al., 2011).

A quadratic equation was used to establish the relationship between the UASE parameters (X_1 = ultrasound power, X_2 = extraction temperature, X_3 = sonication time) and the DRBS gamma oryzanol recovery (Y) as shown in Equation 7:

$$Y = 94.595+2.641X_1+4.698X_2+4.410X_3-1.212X_1*X_3 -3.360X_2^2-2.559X_3^2 \quad (7)$$

Table 2 Experimental and predicted gamma oryzanol recovery under variable ultrasound powers (X_1), extraction temperatures (X_2) and sonication times (X_3)

Run	Coded variable						Experimental value	Predicted value
	X_1	X_2	X_3	X_1(W/g)	X_2(°C)	X_3(min)	(%)	(%)
1	1-	1-	1-	05.	35	4	7321.	7292.
2	1	1-	1-	45.	35	4	8289.	8237.
3	1-	1	1-	05.	55	4	8612.	8590.
4	1	1	1-	45.	55	4	9199.	9189.
5	1-	1-	1	05.	35	26	8637.	8604.
6	1	1-	1	45.	35	26	9082.	9061.
7	1-	1	1	05.	55	26	9556.	9531.
8	1	1	1	45.	55	26	9646.	9642.
9	1-	0	0	05.	45	15	9020.	9096.
10	1	0	1-	45.	45	15	9527.	9624.
11	0	1-	0	25.	35	15	8518.	8654.
12	0	1	0	25.	55	15	9519.	9594.
13	0	0	1-	25.	45	4	8650.	8763.
14	0	0	1	25.	45	26	9584.	9645.
15	0	0	0	25.	45	15	9527.	9459.
16	0	0	0	25.	45	15	9527.	9459.
17	0	0	0	25.	45	15	9671.	9458.

Table 3 ANOVA results of response surface quadratic model for gamma oryzanol recovery

Source	Degree of freedom	Sum of squares	Mean square	F value	*p*-value
Total corrected	16	659750.	41234.		
Regression	9	648634.	72071.	45385.	0000.
Residual	7	11116.	15879.		
Lack of fit	5	9733.	1947.	2816.	0283.
Pure error	2	0691.	0691.		

R^2 = coefficient of determination = 0.983; adjusted R^2 = 0.961; Model predictive ability Q^2 = 0.933; $p < 0.05$ indicates statistical significance

Effect of ultrasound-assisted solvent extraction parameters on gamma oryzanol recovery

In Table 4, the linear terms X_1, X_2 and X_3, the interaction terms X_1X_3 and the quadratic terms X_2^2 and X_3^2 affected the DRBS gamma oryzanol recovery. The interaction terms X_1X_2 and X_2X_3 and the quadratic term X_1^2 had no significant effect on the gamma oryzanol recovery and were eliminated.

Table 4 Regression coefficients and p-values of model terms after backward elimination

Source [a]	Regression coefficient	*p*-value[b]
Constant	94595.	0000.
X_1	2641.	0000.
X_2	4698.	0000.
X_3	4410.	0000.
X_1* X_3	-1.212	0050.
X_2^2	-3.360	0003.
X_3^2	-2.559	0011.

X_1, X_2, X_3 = ultrasound power (W/g), extraction temperature (°C), and sonication time (min), respectively; *p*-value < 0.05 indicates significant difference

Fig. 1A illustrates the interaction effect between ultrasonic power (X_1) and extraction temperature (X_2) on the gamma oryzanol recovery, given a 15 min sonication time (X_3). The recovery increased with increases in X_1 and X_2, achieving the maximum recovery (96.98%) at 4.5 W/g and 49°C. For X_1 of 4.5 W/g, the gamma oryzanol recovery decreased as X_2 increased. This could be attributed to the degradation of gamma oryzanol by the high extraction temperature.

In Fig. 1B, X_1 and X_3 had a significant impact on the DRBS gamma oryzanol recovery. The maximum gamma oryzanol recovery (97.15%) was achieved with X_1 at 4.5 W/g and X_3 at 19.40 min, given X_2 was 45°C. The gamma oryzanol recovery slightly decreased (96.90%) as the sonication time increased from 19.40 min to 26 min, given 4.5 W/g ultrasound power. This could be attributed to the fact that high ultrasound power and an extended sonication time increased temperatures and pressure, resulting in turbulence in the medium and subsequent microstructure disintegration (Balachandran et al., 2006; Zhang et al., 2008).

In Fig. 1C, the maximum gamma oryzanol recovery (97.59%) was achieved at X_2 of 50.30°C and X_3 at 21.54 min, given X_1 was 2.5 W/g. According to Sharma and Gupta (2006) and Zhang et al. (2008), high extraction temperatures and an extended sonication time enhanced the mass liquid transfer (induced by cavitation forces), resulting in increased extraction yields. On the contrary, in the current study, high extraction temperatures (51–55°C) and extended sonication times (22–26 min) contributed to lower levels of gamma oryzanol recovery. A similar finding was also reported for ultrasonic pretreatment combined with cold-press extraction on the gamma oryzanol content of rice bran oil (Phan et al., 2018).

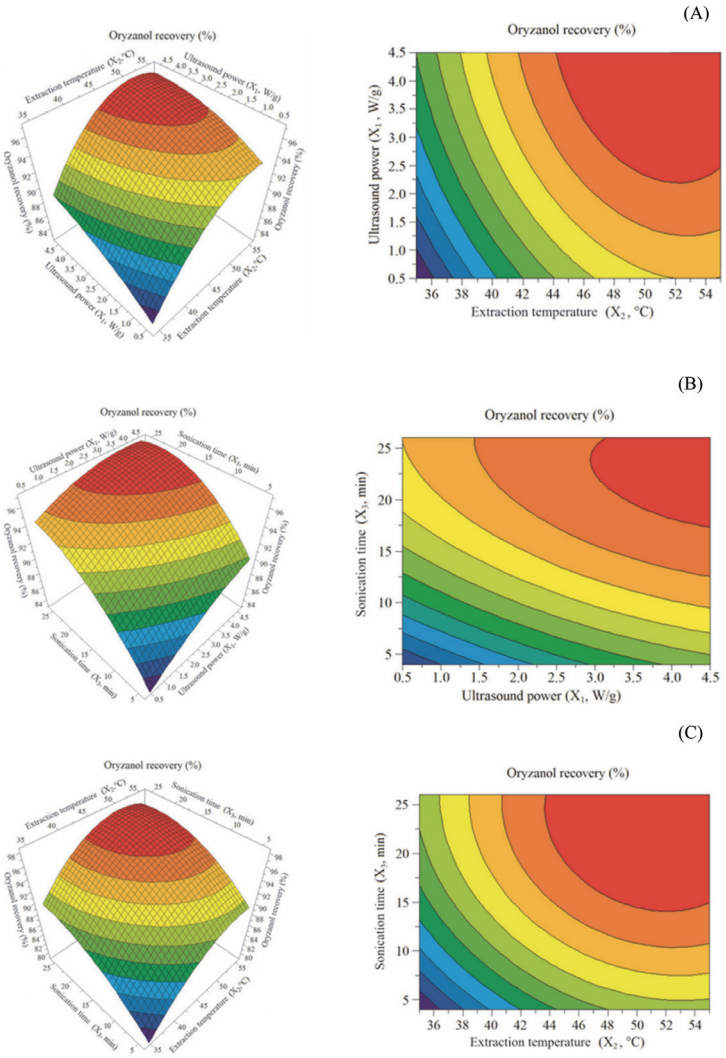

Fig. 1 Response surface plots of relationships between gamma oryzanol recovery and ultrasound power, extraction temperature and sonication time, given: (A) sonication time of 15 min; (B) extraction temperature of 45°C; (C) ultrasound power of 2.5 W/g

Optimization of gamma oryzanol extraction

The optimal UASE conditions were 4.0 W/g ultrasound power, 50°C extraction temperature and 21.50 min sonication time, achieving 98.15% gamma oryzanol recovery. Under the optimal conditions, the predicted gamma oryzanol recovery was 98.03%, indicating good agreement between the experimental and predicted values. In essence, the response model could be used to optimize the UASE parameters for enhanced gamma oryzanol recovery.

Furthermore, HPLC was utilized to characterize the chemical composition of DRBS gamma oryzanol extracted under the optimal UASE conditions and the results were compared with the gamma oryzanol standard. Figs. 2 and 3 illustrate the HPLC chromatograms of the standard and DRBS gamma oryzanol, respectively, both consisting of four peaks: campesteryl ferulate (retention time (RT) =

7.753 min and 7.765 min), 24-methylene cycloartanyl ferulate (RT = 7.050 min and 7.065 min), *β*-sitosteryl ferulate (RT = 9.006 min and 8.989 min) and cycloartenyl ferulate (RT = 6.235 min and 6.243 min), respectively. The chemical composition of the gamma oryzanol standard and DRBS were similar, consistent with Kumar et al. (2009) and Sakunpak et al. (2014).

Microstructure of rice bran soapstock

Figs. 4A–B illustrate the microstructure of DRBS and optimally UASE-treated DRBS, respectively. In Fig. 4A, the microstructure of DRBS was irregularly spherical and heterogeneous in size due to the stickiness of the soapstock. This was consistent with Lamas et al. (2016), who reported that the microstructure of rice bran soapstock is non-uniform due to its sticky characteristic.

In Fig. 4B, the formation of dented surfaces on the soapstock particles after sonication enhanced the extraction efficiency. In addition, the ultrasound treatment increased the porosity and thus the extraction efficiency. The finding was consistent with (Phan et al., 2018), who reported that ultrasonic treatment induced structural changes, fissures and cavities.

Kinetics of ultrasound-assisted solvent extraction process

The extraction kinetics were examined to characterize the effects of the UASE parameters (ultrasound power and extraction temperature) on DRBS gamma oryzanol recovery, given sonication times of 0–21.50 min and 85:15% (v/v) ethyl acetate-to-ethanol mixture. Fig. 5A illustrates the simulated and experimental DRBS gamma oryzanol concentrations under different ultrasound power levels (0.5 W/g, 2.5 W/g, 4.5 W/g) relative to sonication time, given an extraction temperature of 45°C. Fig. 5B depicts the concentrations under different extraction temperatures (35°C, 45°C, 55°C) relative to sonication time, given an ultrasound power of 2.5 W/g.

In Figs. 5A–B, the simulated gamma oryzanol concentrations agreed with the experimental data, indicating the validity of the second-order kinetic model. In addition, the kinetic results (simulation and experimental) revealed that two-thirds of the gamma oryzanol (>3.0 g/L) was recovered in the early sonication stage (0–8 min). Extended sonication time (from 8 min to 21.50 min) slightly increased the yield, except at 55°C and 21.5 min where the gamma oryzanol concentration slightly decreased (Fig. 5B), consistent with the RSM results (Fig. 1C).

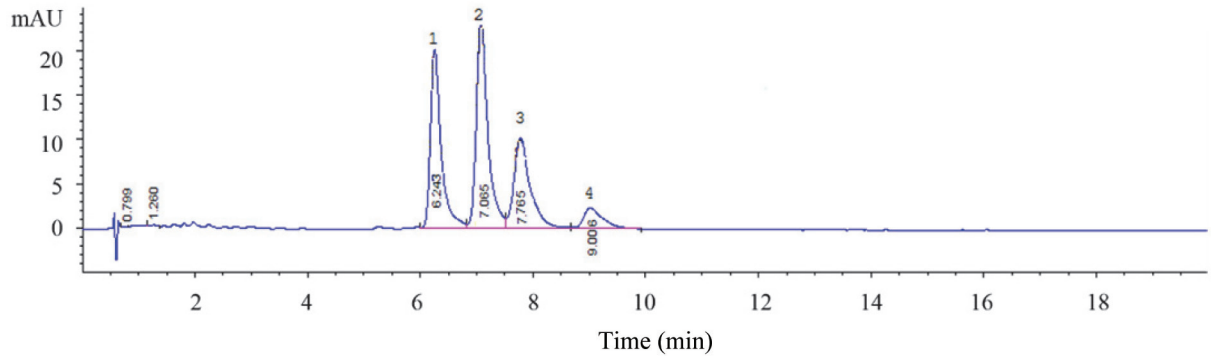

Fig. 2 HPLC chromatogram of standard gamma oryzanol, where 1 = cycloartenylferulate, 2 = 24-methylenecy cloartanyl ferulate, 3 = campesterylferulate, 4 = *β*-sitosteryl ferulate

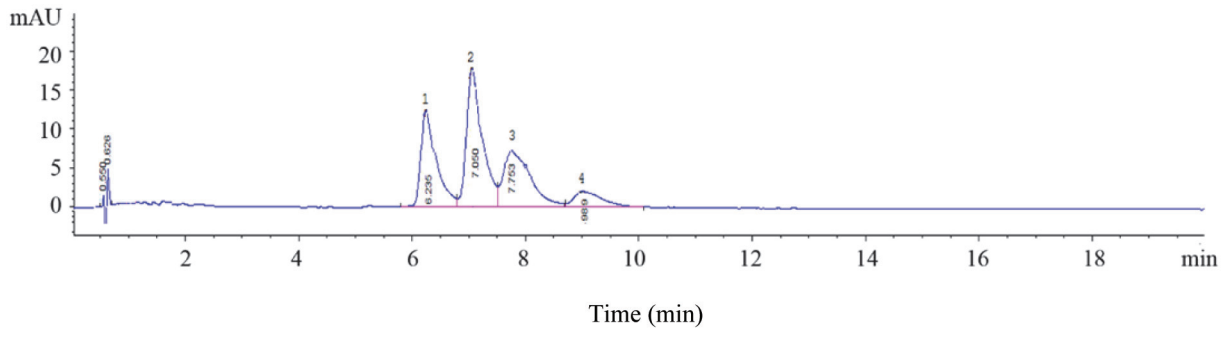

Fig. 3 HPLC chromatogram of dried rice bran soapstock gamma oryzanol, where 1 = cycloartenylferulate, 2 = 24-methylenecy cloartanyl ferulate, 3 = campesterylferulate, 4 = *β*-sitosteryl ferulate

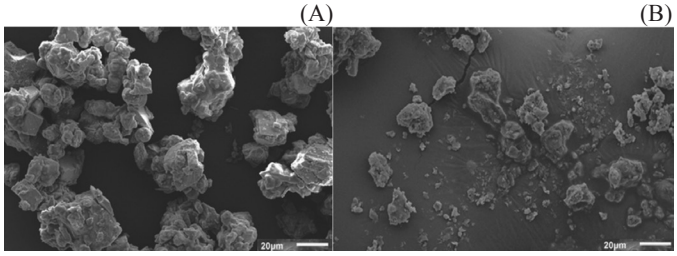

Fig. 4 Scanning electron microscopy images: (A) dried rice bran soapstock (DRBS); (B) treated DRBS using ultrasound-assisted solvent extraction for response surface method-based optimal conditions (4.0 W/g, 50°C, 21.5 min)

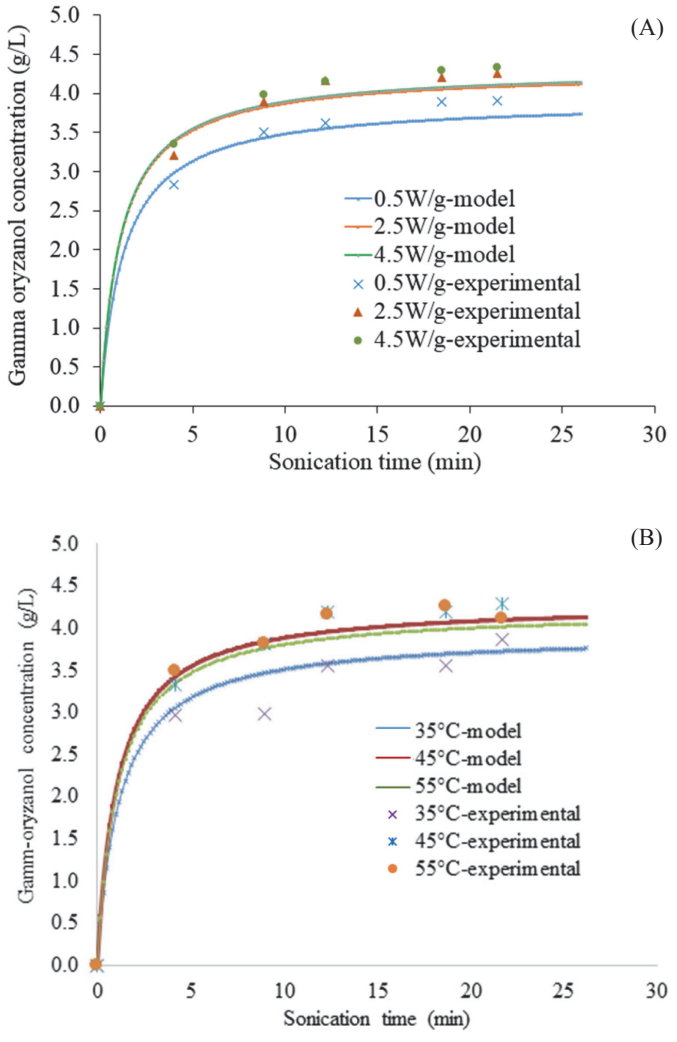

Fig. 5 Gamma oryzanol concentration relative to sonication time given: (A) extraction temperature of 45°C; (B) ultrasound power of 2.5 W/g

Specifically, in Fig. 5A, gamma oryzanol concentrations significantly increased with increased ultrasound power from 0.5 W/g to 2.5 W/g but there was no significant increase with increasing the ultrasound intensity from 2.5W/g to 4.5W/g. According to Phan et al. (2018), high ultrasound power enhanced the mass transfer process and the recovered yield. In addition, gamma oryzanol concentrations increased significantly as the extraction temperature increased from 35°C to 45°C. According to Lazar et al. (2016), higher extraction temperatures using ultrasound-assisted extraction improved the extraction rates of polyphenolic compounds because under higher temperatures, the solubility and diffusivity of phenolic compounds increased, enhancing the mass transfer and accelerating the extraction process. However, at 55°C and 21.50 min sonication time, although there was a decrease observed in the gamma oryzanol concentration, it was not significant.

Fig. 6A illustrates the simulated and experimental extraction rate reciprocal of DRBS gamma oryzanol concentrations under variable ultrasound power levels (0.5 W/g, 2.5 W/g, 4.5 W/g) relative to sonication time, given an extraction temperature of 45°C. Fig. 6B depicts DRBS gamma oryzanol concentrations under variable extraction temperatures (35°C, 45°C, 55°C) relative to sonication time, given an ultrasound power of 2.5 W/g. The gamma oryzanol concentration at saturation (C_s) and extraction rate constant (k) were the slope and intercept, respectively, of the plots. The initial extraction rate (h) was calculated using Equation 6.

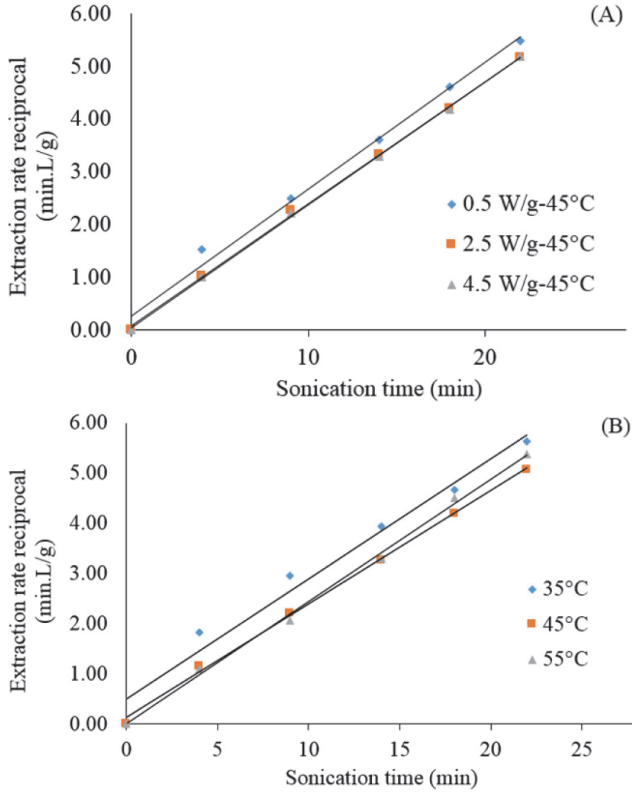

Fig. 6 Extraction rate reciprocal of dried rice bran soapstock gamma oryzanol recovery relative to sonication time given: (A) extraction temperature of 45°C; (B) ultrasound power of 2.5 W/g

Table 5 tabulates the kinetic parameters of the second-order kinetic extraction model. C_s, k and h *increased with increases in* ultrasound power (from 0.5 W/g to 4.5 W/g) and extraction temperature (from 35°C to 45°C). C_s and h *decreased when the extraction temperature rose from 45*°C *to 55°C.* The kinetic results indicated that the extraction efficiency of UASE improved with high ultrasound power (4.5 W/g) and moderate extraction temperature (45°C), given a 21.50 min sonication time. Based on Table 5, given the R^2 values of 0.972–0.997 and root mean square error (RSME) values of 0.091–0.214, the second-order kinetic model was suitable for characterizing the effect of UASE parameters on DRBS gamma oryzanol recovery.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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Table 5 Kinetic parameters of dried rice bran soapstock gamma oryzanol recovery under different ultrasound powers and extraction temperatures, given 21.5 min sonication time

Kinetic parameter	Ultrasound power (W/g)			Extraction temperature (°C)		
	0.5	2.5	4.5	35	45	55
C_s (g/L)	3.841	4.251	4.330	3.724	4.195	3.986
k (L/g.min)	0.207	0.215	0.215	0.193	0.216	0.217
h (g/L.min)	3.165	3.975	3.994	2.920	4.025	3.863
R^2	0.977	0.997	0.996	0.972	0.996	0.996
RMSE	0.0907	0.0912	0.0989	0.1136	0.1736	0.2134

C_s = gamma oryzanol concentration at saturation; k = extraction rate constant; h = initial extraction rate; R^2 = coefficient of determination; RMSE = root mean square error