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MICROWAVE-ASSISTED EXTRACTION OF "CẨM" PURPLE RICE BRAN POLYPHENOL: A KINETIC STUDY

Le Thi Kim Loan[1✉], Ngo Van Tai[2], Nguyen Minh Thuy[3]

[1]Faculty of Agriculture and Food Technology, Tien Giang University
Tien Giang Province, **Vietnam**
[2]School of Food Industry, King Mongkut's Institute of Technology Ladkrabang
Bangkok 10520, **Thailand**
[3]Institute of Food and Biotechnology, Can Tho University
Can Tho, **Vietnam**

ABSTRACT

Background. "Cẩm" rice bran has been considered a waste product; however, it possesses rich bioactive compounds. These compounds could be utilized to make value-added products, using microwave-assisted extraction.

Materials and methods. This study aimed to investigate and establish the kinetic extraction for "Cẩm" rice bran under different conditions of microwave-assisted extraction. Five levels of microwave power (90, 150, 300, 600, and 800 W) were used for extraction at a time range from 0 to 30 minutes. The extraction yield (%) and total phenolic compound (mg gallic acid equivalent per g, mgGAE/g) were determined. The experimental data were fitted with five empirical models to find the best fit model.

Results. The power of irradiation greatly influenced the extraction yield and phenolic compounds in rice bran extract. The fast rate of extraction was found at the initial stage (after 5 minutes of extraction), then remained unchanged or slightly declined. Among the five models, the first-order model showed the best fit between the actual and predicted data.

Conclusions. Based on the extraction rate constant from the first-order model, 500 W was considered the appropriate power level for extracting polyphenol from rice bran with a high yield of extraction and total polyphenol content. These conditions could be further optimized and upscaled for use in the food industry.

Keyword: microwave-assisted extraction, rice bran, polyphenol, antioxidant, waste

INTRODUCTION

Rice is one of the most important staple foods around the world. In Vietnam, various rice varieties are cultivated and produced annually. However, rice production produces a large amount of waste in Vietnam, which could be utilized to create a value-added product (Van Tai et al., 2023). One of the waste products from rice production is rice bran. Recent research has shown that rice bran contained various nutrients, as well as antioxidant compounds (Huang and Lai, 2016). The presence of significant amounts of bioactive substances, including dietary fiber, tocopherols, tocotrienols, oryzanols, phytic acid, and phenolic compounds, is usually thought to be responsible for quality of rice (Arab et al., 2011; Thuy et al., 2021; 2022a). These bioactive compounds could potentially reduce the glycemic index and antidiabetic activity (Ngo et al.,

✉lethikimloan@tgu.edu.vn, https://orcid.org/0000-0001-7472-8334

2022). The rice bran also possesses a large content of vitamins and nutrients (Thuy et al., 2022a).

"Cẩm" rice, which originated in Tien Giang province (Vietnam), has a purple outer layer and is commonly used for cooking or producing various products such as instant rice, germinated rice flour, or gluten-free bread (Loan et al., 2021; Le et al., 2022; Le and Nguyen, 2019; Loan et al., 2023b). However, after the milling and polishing process, the "Cẩm" rice bran is also discharged and not properly used. Recently, the study of Loan et al. (2023a) reported that "Cẩm" rice bran could be utilized for a value-added product because of its high protein content and other nutrients. Another study also showed that these rice varieties have a high anthocyanin content, which accounted for 46.3 mg/100g (Loan et al., 2023b). Due to the potential of high antioxidants compounds in "Cẩm" rice bran, the study was limited to Vietnam. The extraction process for utilization of this material should be conducted. Recently, the microwave-assisted extraction process was an emerging trend to utilize various food waste materials such as peach waste (Kurtulbaş et al., 2022), aloe vera skin (Solaberrieta et al., 2022), and coffee pulp waste (Tran et al., 2022). This method also considered new green energy-saving technologies and presented several advantages, compared to conventional technologies: increase of the extraction kinetics, a shorter extraction time and rapid temperature increase, and a higher efficiency and extraction yield (Alvi et al., 2022). Therefore, the aim of this study was to investigate the effect of different microwave-assisted conditions on the extraction of polyphenol from Cẩm rice bran by using kinetic analysis. This study could be fundamental knowledge for further optimizing the process on a large scale.

MATERIAL AND METHOD

Materials

Cẩm rice bran was collected after the milling and polishing process at a local company in Tien Giang province (Vietnam). The defatted rice bran was milled to pass through an 80 mesh sieve for further extraction (Surin et al., 2020). The powder was kept in a dark airtight bag at 4°C until the extraction was conducted.

Extraction process

Different levels of microwave power (90, 150, 300, 600, and 800 W) were used for this extraction experiment. An electric microwave oven (Electrolux, Korea) was used for operating the extraction process. Extractions were performed at a solid–liquid ratio of 1:10 (w/v). The solvent used for extraction was 60% ethanol (food grade) (Van Tai et al., 2021). The crude extracts were immediately centrifuged at 10,000 rpm for 1 min and filtered through filter paper under a vacuum (V-700, Büchi, Switzerland) immediately after extraction. The extracts were collected in glass vials and stored at 4°C until further analysis. Crude liquid extract was vacuum-evaporated and further dried to determine the total extraction yield. The results were expressed as the percentage of total extractable solids per 100 g of dry sample (%, w/w).

The dried extract was dissolved again with 80% methanol before using it for total phenolic content (TPC) analysis. The total phenolic content of the extract was determined according to the method described by Wanyo et al. (2014). 300 µL of extract was mixed with 2.25 mL of Folin–Ciocalteu reagent (10%) and allowed to stand at room temperature for 5 min; 2.25 mL of sodium carbonate (60 g/L) solution was added to the mixture. After 90 min at room temperature, absorbance was measured at 725 nm using a spectrophotometer. The results were expressed as mg gallic acid equivalents in 1 g of dried sample (mg GAE/g).

Kinetic modelling of the MAE of TPC and extraction yield of Cẩm rice bran

In the present study, five mathematical models were used to fit the experimental data of TPC and extraction yield (Table 1). These models were used for the extraction kinetics study of plant materials (Kayahan and Saloglu, 2020; Kurtulbaş et al., 2022; Pavlić et al., 2023). The fitness of the model would be based on the coefficient determination (R^2 value).

RESULTS AND DISCUSSION

Effect of extraction conditions on the yield of extraction and polyphenol content

Microwave time and energy level strongly affect the extraction ability and polyphenol content in the extract from "Cẩm" rice bran (Fig. 1–2). After 5 minutes of

Table 1. Selection model for this study

Model name	Model equation	Reference
First-order model	$C_t = C_{eq}(1 - e^{-kt})$	(Yedhu Krishnan and Rajan, 2016)
Second-order model	$C_t = C_{eq}t/(k + t)$	(Harouna-Oumarou et al., 2007)
Elovich’s model	$C_t = E \ln(t) + a$	(Dong et al., 2014)
Power-law model	$C_t = Bt^n$	(Dong et al., 2014)
Peleg’s model	$C_t = t / (k_1 + k_2t)$	(Kayahan and Saloglu, 2020)

Note: C_t is the solute concentration of TPC (mg GAE/g) or extraction yield (%) at time (t); C_{eq} is its concentration at equilibrium; k, k_1, k_2, E, a, B, n are model constants.

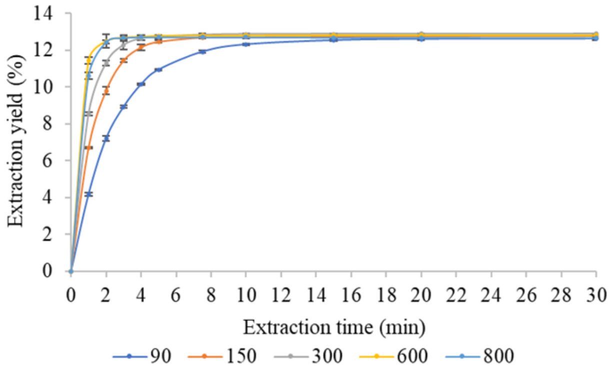


Fig. 1. The change of extraction yield at different extraction conditions

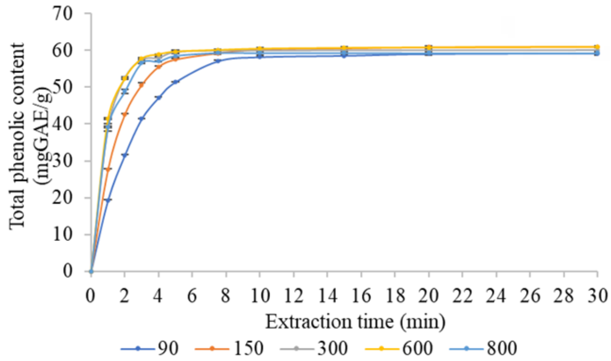


Fig. 2. The change of total phenolic content under different extraction conditions

extraction, the polyphenol content and the amount of extracted solution increased remarkably. In particular, at the power level above 300 W, the obtained extraction yield was about 12.5%, and the polyphenol content reached approximately 60 mg GAE/g. Pavlić et al. (2023) also reported that at the initial stage of microwave-assisted extraction (MAE), the polyphenol, flavonoid, and extraction yield rose greatly. However, at the later stage of extraction (after 15 mins), the extraction yield and polyphenol content remained almost the same or slightly decreased when the time of extraction was prolonged. There was no significant difference between the different levels of microwave power after 15 mins of extraction (Table 2).

The crucial step in obtaining antioxidants and polyphenolic compounds from plant sources is extraction. In recent years, collecting polyphenolic components and antioxidants from industrial by-products has attracted a lot of interest through the use of microwave-assisted extraction (MAE) (Ruiz-Aceituno et al., 2016). Many factors, including extraction duration, solvent type, solvent/solid ratio, and power, can

Table 2. The extraction yield and total phenolic content after 15 min of extraction at different levels of microwave power

Parameters	Microwave power (W)				
	90	150	300	600	800
TPC, mg GAE/g	58.60 ±0.59	60.63 ±0.61	60.13 ±0.60	60.69 ±0.61	59.35 ±0.59
Extraction yield, %	12.54 ±1.24	12.75 ±1.27	12.88 ±1.29	12.82 ±1.28	12.70 ±1.27

Values are experessed as mean ±STD (standard deviation).

be controlled to affect how efficiently and effectively phenolic compounds are extracted using the MAE method (Thuy et al., 2022c). The research of Kayahan and Saloglu (2020) showed that an extraction time of 6 min was appropriate to extract the phenolic and antioxidant compounds from Turkish artichoke. The structure of the material was changed because of the microwave effect that could have led to an increase in the extraction yield. However, when the extraction yield reached equilibrium, the yield remained unchanged or might have degraded because of heat and oxidation (Thuy et al., 2022b; Van Tai et al., 2021; Zhang et al., 2013). The release of additional heat produced by microwaves and utilized as the activation energy for various degradation activities may be the cause of the decomposition of bioactive compounds during MAE (Périno-Issartier et al., 2011).

Mathematical modeling of "Cẩm" rice bran microwave-assisted extraction

The data from Figures 1 and 2 were fitted by the four empirical models and the results of model constants and regression variables are presented in Tables 3 and 4. In terms of rice bran extraction yield, the model constants fluctuated with the change of microwave power during extraction. The mean value of the coefficient of determination was highest when fitted with the first order model, while the lowest value was found when experimental data were fitted with a power-law model. The second-order model and Peleg model also showed a relatively high R^2 value. The average vertical distance between the experimental points and the fitted curve decreases as a result. Therefore, the first-order model could give the best fit for kinetic extraction yield of rice bran extract by MAE, which can be seen in Figure 3. Furthermore, the results from Table 3 also show the remarkable increase in k value (extraction rate constant) when the microwave power level increased from 90 to 600 W. However, this value decreased significantly when the extraction was conducted at 800 W. The extraction solvent's polarity, viscosity, and surface tension were altered by the irradiation power, resulting in a greater release of solutes from plant cells (Mustapa et al., 2015). However, increasing microwave power resulted in the degradation of antioxidant molecules, which led to a reduction in the yield of extraction (Tena and Asuero, 2022).

Table 3. MAE kinetics of extraction yield by various models

Model	Power level (W)	k	C_{eq}	R^2	MSE
1	2	3	4	5	6
$C_t = C_{eq}(1 - e^{-kt})$	90	k = 0.5077	C_{eq} = 12.6138	99.41	0.0137
	150	k = 1.0948	C_{eq} = 12.7812	99.84	0.0082
	300	k = 1.9640	C_{eq} = 12.8349	99.78	0.0181
	600	k = 8.3089	C_{eq} = 12.7830	97.51	0.3605
	800	k = 5.0590	C_{eq} = 12.7199	99.71	0.0364
	Mean			99.25	0.0874
$C_t = C_{eq}t/(k + t)$	90	k = 1.7748	C_{eq} = 14.0821	98.64	0.2544
	150	k = 0.7915	C_{eq} = 13.7309	98.19	0.3176
	300	k = 0.4561	C_{eq} = 13.5197	98.92	0.1829
	600	k = 0.1159	C_{eq} = 13.0071	99.89	0.0184
	800	k = 0.1737	C_{eq} = 1.3020	99.44	0.0907
	Mean			99.02	0.1728

Table 3 – cont.

1	2	3	4	5	6
$C_t = E \ln(t) + a$	90	E = 2.4502	a = 5.8769	86.18	1.2370
	150	E =1.5245	a = 8.8559	68.32	1.3848
	300	E = 0.9990	a = 10.3648	60.67	0.8309
	600	E = 0.2930	a = 12.0953	53.91	0.0943
	800	E = 0.3962	a = 11.7471	41.46	0.2847
	Mean			62.11	0.7663
$C_t = Bt^n$	90	B = 6.8391	n = 0.2156	77.66	1.9993
	150	B = 9.2717	n = 0.1208	62.54	1.6372
	300	B = 10.5527	n = 0.0774	56.97	0.9092
	600	B = 12.1127	n = 0.0228	52.86	0.0964
	800	B = 11.7830	n = 0.0308	40.11	0.2913
	Mean			58.03	0.9867
$C_t = t / (k_1 + k_2t)$	90	$k_1 = 0.1260$	$k_2 = 0.0710$	98.64	0.2544
	150	$k_1 = 0.0576$	$k_2 = 0.0728$	98.19	0.3176
	300	$k_1 = 0.0337$	$k_2 = 0.0740$	98.91	0.1829
	600	$k_1 = 0.0089$	$k_2 = 0.0769$	99.89	0.0184
	800	$k_1 = 0.0133$	$k_2 = 0.0768$	99.44	0.0907
	Mean			99.01	0.1728

The coefficient of determination of TPC content in rice bran extract when applied to four different models also shows the same trend with extraction yield. The R^2 value was followed by 98.79 (first-order model) > 98.74 (second-order model and Peleg model) > 70.60 (Elovich model) > 65.16 (power-law model). Therefore, the first-order model also gave the best fit between actual and predicted data, which is presented in Figure 3. However, it also showed that before it reached the equilibrium, the predicted value was slightly higher than the experimental value.

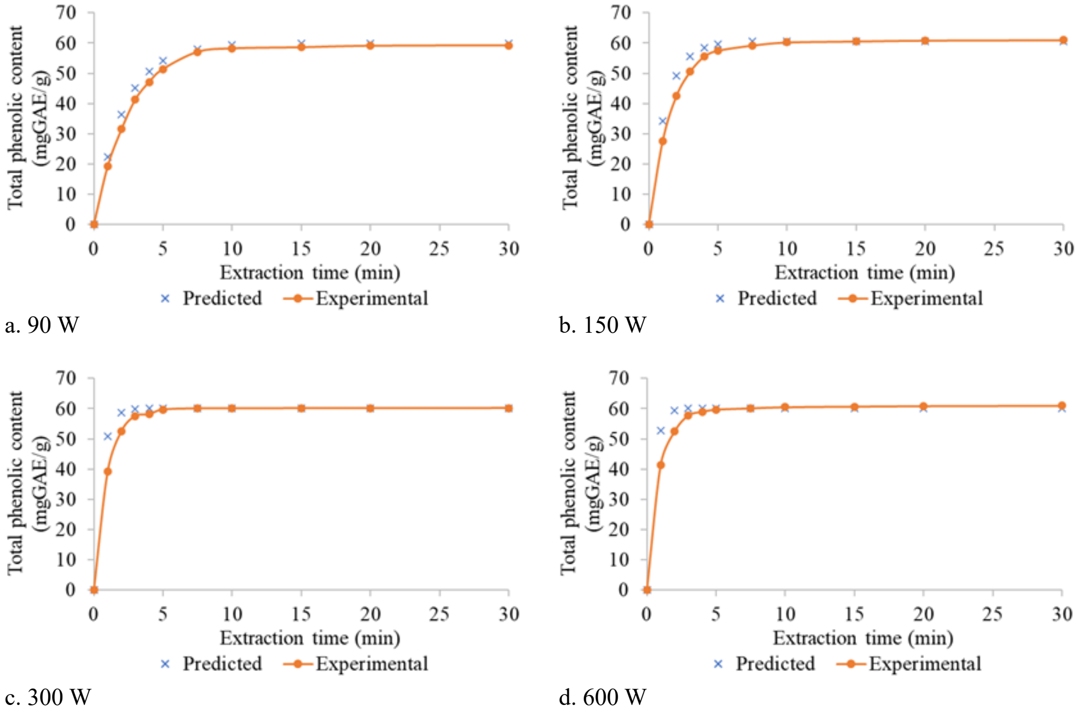
Table 4. MAE kinetics of yield of polyphenol by various models

Model	Power level (W)	Model constant		R^2	MSE
1	2	3	4	5	6
$C_t = C_{eq} (1 – e^{-kt})$	90	k = 0.4702	$C_{eq} = 5.9844$	98.93	0.0051
	150	k = 0.8330	$C_{eq} = 6.0678$	99.81	0.0017
	300	k = 1.8722	$C_{eq} = 6.0086$	99.96	0.0008
	600	k = 2.0806	$C_{eq} = 6.0233$	97.31	0.0508
	800	k = 1.7610	$C_{eq} = 5.9053$	97.94	0.0353
	Mean			98.79	0.0187

Table 4 – cont.

1	2	3	4	5	6
$C_t = C_{eq}t/(k + t)$	90	k = 1.8900	C_{eq} = 6.6736	98.16	0.0780
	150	k = 1.0558	C_{eq} = 6.6074	98.41	0.0650
	300	k = 0.4739	C_{eq} = 6.3236	98.82	0.0436
	600	k = 0.4419	C_{eq} = 6.3445	99.31	0.0257
	800	k = 0.5043	C_{eq} = 6.2398	99.02	0.0351
	Mean			98.74	0.0495
$C_t = E \ln(t) + a$	90	E =11.8902	a = 26.6378	85.42	31.0095
	150	E = 8.8553	a = 37.4940	76.13	31.5891
	300	E = 4.8114	a = 48.0263	60.68	19.2687
	600	E = 4.6520	a = 48.8730	65.59	14.5826
	800	E = 5.0257	a = 46.5568	65.17	17.3402
	Mean			70.60	22.7580
$C_t = Bt^n$	90	B = 3.1484	n = 0.2228	76.60	0.4975
	150	B = 4.0268	n = 0.1515	69.26	0.4068
	300	B = 4.8959	n = 0.0798	56.86	0.2114
	600	B = 4.9696	n = 0.0770	61.98	0.1612
	800	B = 4.7551	n = 0.0851	61.12	0.1936
	Mean			65.16	0.2941
$Ct = t / (k_1 + k_2t)$	90	k_1 = 0.0283	k_2 = 0.0150	98.16	7.8007
	150	k_1 = 0.0159	k_2 = 0.0151	98.41	6.4993
	300	k_1 = 0.0075	k_2 = 0.0158	98.82	4.3574
	600	k_1 = 0.0069	k_2 = 0.0158	99.31	2.5683
	800	k_1 = 0.0081	k_2 = 0.0160	99.02	3.5120
	Mean			98.74	4.9475

The extraction rate also increased when the microwave power level rose to 600 W. The decline trend was found when an increase in power was conducted. The results are similar to the study by Filip et al. (2017), who reported that increasing the irradiation power did not significantly increase the polyphenol yield when applying MAE to coriander seeds and basil leaves. A further rise in yield at later stages of extraction may be caused by the release of bound polyphenols, while the decrease in k value at 800W may be explained by the quick denaturation of certain compounds at the start of the MAE process due to high energy and heating. The irradiation power has a big impact on k, but less of an impact on the response's asymptotic value. The bioactive compound in peppermint essential oil decomposed when MAE was treated for longer than 30 minutes (Dai et al., 2010). It is possible that some polyphenol compounds may degrade when the sample is exposed to microwaves for an excessively extended period of time (Xiao et al., 2008). By applying the cubic spine model, the predicted maximum extraction rate was found to be approximately 2.4 min^{-1} when the microwave power use was at about 500 W (Fig. 4). Further optimization processes could be considered in this condition.



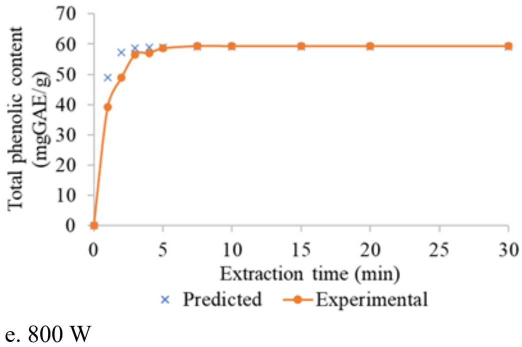


Fig. 3. The correlation between experimental and predicted TPC by applying first-order model

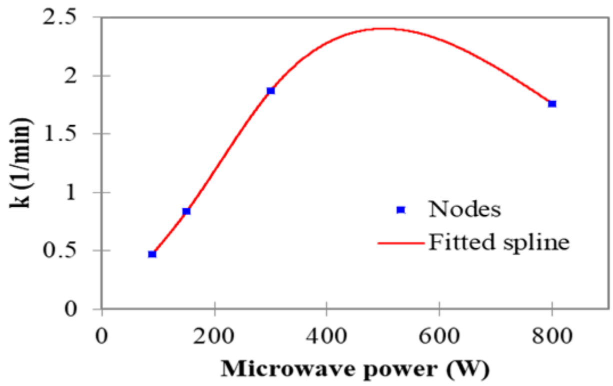


Fig. 4. The impact of microwave power on extraction rate of TPC from “Cẩm” rice bran by cubic spline model

CONCLUSION

Microwave-assisted extraction could be used for recovering polyphenols from "Cẩm" rice bran. The yield of extraction and total phenolic compound in the extract were approximately 12% and 60 mg GAE/g, respectively. The first-order kinetic was shown to be the best fit to predict the extraction yield and total phenolic compound at different conditions of extraction. The results also show that the level of microwave power at 500 W could be the appropriate conditions for further optimization. In addition, this extract could also be utilized in various products, as well as providing health benefits.

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