Process intensification and kinetic studies of ultrasound-assisted extraction of flavonoids from peanut shells

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A B S T R A C T

In this work, extraction of flavonoids from peanut shells has been studied in the presence of ultrasound and the results are compared with Soxhlet and heat reflux extraction for establishing the process intensification benefits. The process optimization for understanding the effects of operating parameters, such as ethanol concentration, particle size, solvent to solid ratio, extraction temperature, ultrasonic power and ultrasonic frequency, on the extraction of flavonoids has been investigated in details. The highest extraction yield (9.263 mg/g) of flavonoids was achieved in 80 min at optimum operating parameters of particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic power of 120 W and ultrasonic frequency of 45 kHz with 70% ethanol as the solvent. Two kinetic models (i.e. phenomenological model and Peleg’s model) have been introduced to describe the extraction kinetic of flavonoids by fitting experimental data and predict kinetic parameters. Good performance with slight loss of goodness of fit of two models was found by comparing their coefficient of determination (R²), root mean square error (RMSE) and/or mean percentage error (MPE) values. This work would provide the reduction of degradation and the economic evaluation for the extraction processes of flavonoids from peanut shells, as well as give a better explanation for the mechanism of ultrasound.

1. Introduction

Peanut (Arachis hypogaea L.), being classified an annual legume plant, is a very important source of food and edible oil all over the world [1]. Peanut shell is a major waste by-product after peanut processed, and 60 million tons of the world annual production of peanuts may produce more than 18 million tons of shells, and the quantity is still increasing according to previous reports [2,3]. Only a small quantity of peanut shells are made into cattle feed, whereas the rest of the vast majority of peanut shells are usually used as fuel for cooking and heating, and even discarded as a waste, which may lead to environmental pollution and waste of resources [4]. Many investigations have shown that peanut shell is a complex combination of organic compounds with flavonoids content from 0.25% to 1.42% in different peanut shell samples from different maturities and varieties [5,6]. The main ingredients in flavonoids including 5, 7-dihydroxychromone, luteolin and luteolin are known to have various physiological activities i.e. vasodilation, anti-inflammatory, cancer prevention and antioxidant [7], as well as exhibit other biological activities such as antiviral and antibacterial properties [8,9]. Thus, there is renewed interest in the extraction of flavonoids from peanut shells to develop higher added-value products.

For extraction of flavonoids as well as other flavonoids components from fruits and rhizomes of legume plants, different extraction methods including conventional solvent extraction, Soxhlet extraction, heat reflux extraction, continuous-flow microextraction, Enzyme-assisted extraction have been already reported in the literature [3,10–13]. Moreover, advanced extraction methods based on microwave assisted extraction [14], supercritical carbon dioxide extraction [10], high voltage electrical discharges extraction [15], ultrasound-assisted extraction [16,17] and ultrasound-assisted enzymatic extraction [18] have also been investigated. Conventional extraction methods used for the solvent extraction of plant materials have been proved to be the drawbacks of longer extraction time, higher temperature and lower extraction efficiency, particularly negative effect on natural components due to usage of large amount of organic solvents and higher energy consumption [19]. Furthermore, some natural components such as flavonoids with thermal instability may be degraded during thermal extraction [20,21]. Therefore, in order to overcome these disadvantages associated with conventional extraction methods as well as consider the low level of flavonoids present in peanut shells and their complexity,
looking for the efficient, robust and economical extraction based on ultrasound as a process intensification approach is of great importance and necessary.

Ultrasound has been proven to be a very useful approach for increasing the extraction efficiency of bioactive compounds from natural products and improving the mass transfer in liquid medium, which benefits from many advantages of ultrasonic extraction such as reduction in processing time and solvent consumption, usage of lower temperature and higher extraction yield [20–25]. The increased extraction rate is attributed to the phenomenon called acoustic cavitation caused by the propagation of ultrasound pressure waves, which is able to cause plant cell wall and cell membrane to collapse violently, as well reduction in particle size [22,24]. Additionally, some positive effects such as liquid circulation currents and turbulence produced by cavitation make the solvents easier penetrate into cellular materials which lead to significant improvement in the mass transfer rates, so that to promote the enhancement of extraction rate [25–27]. From this point of view and considering for product quality and process efficiency, the first step is to select and optimize the appropriate operating parameters for the extraction of bioactive compounds from plant materials [28]. Then, modelling according to physical or empirical kinetic and optimizing the model parameters can contribute to enhance the extract yield by the further improvement of models.

In recent years, empirical and/or semi-empirical model, a mathematical description for the variation of extract efficiency or yield with operating parameters, has received growing interests due to its useful engineering tool for an economic and fast assessment of various biological treatment processes. Empirical and/or semi-empirical model can also provide a perfect basis for curve fitting, as well as allow representation as a function of process conditions of the extracting plant materials. For these reasons, various empirical models have been successfully used for the assessment of operating parameters effect on the extraction efficiency as well as the description of extraction process [29–33]. However, to our knowledge, little information is available involving modelling and simulation of extraction of flavonoids from peanut shells by ultrasound irradiation. Therefore, it is necessary to evaluate and optimize operating parameters and whole extraction process by mathematical modelling, which can greatly contribute to the utilization of solvent, time and energy, as well as facilitate the optimization and design of extraction processes.

For these purposes, the present work has dealt with the process optimization for understanding the effects of six operating parameters including ethanol concentration, particle size, solvent to solid ratio, temperatures, ultrasonic power and ultrasonic frequency on the extraction of flavonoids. Comparison between the experimental data and the obtained values from the phenomenological model has also been examined. Moreover, to assess the best model for describing the behavior of extraction of flavonoids from peanut shells, the present work introduced the comparison of two well-known empirical models (i.e. phenomenological model and Peleg’s model) to explain the extraction kinetic of flavonoids, which will provide useful information for scale up of the extraction process of flavonoids from peanut shells.

2. Materials and methods

2.1. Plant materials and reagents

Fresh peanuts were obtained from a local market in Yuanzhou district (Jiangxi, China), and remove the shells by hand. The peanut shells were cleaned to remove impurities from the surface and washed three times with water, following dried in a vacuum oven at 55 °C for 36 h till a constant weight. The dried peanut shells were pulverized into powder using a plant crusher and sieved using stainless steel sieves into a range of 0.095–0.995 mm. All powder samples were kept in a desiccator in refrigerator at 5 °C prior to use.

Ethanol solvent (99.5% analytical grade) and Petroleum ether (60–90 °C, analytical grade) used in the extraction experiments were purchased from the Tianjin Chemical Factory (Tianjin, China), 5,7-dihydroxycromone, eriodictyol and Luteolin (99.9%, pharmaceutical grade standard), were obtained from Shanghai Qiangshun Chemical Co. Ltd. (Shanghai, China). Rutin (98.0%, HPLC grade) was available by mail order from the Sigma Chemical Co. Ltd. (St. Louis, MO, USA). Water used for HPLC was purified to be a redistilled one using a Milli-Q Plus system (Millipore, USA). All reagents such as sodium hydroxide, Aluminium nitrate and sodium nitrite were purchased from the Tianjin Chemical Factory (Tianjin, China).

Ultrasound instrument (KQ5200DB) with the function of automatic frequency sweep and power adjustment used for ultrasonic extraction of flavonoids was purchased from the Kunshan Ultrasonic Instrument Co. Ltd. (Jiangsu, China). Ethanol solvent (99.5% analytical grade) used in the extraction experiments were fixed at 10, 15, 30, 40 and 60 ml/g. The mixture was irradiated for 80 min by placing into an ultrasound bath (300 × 240 × 150 mm) with ultrasonic power in the range of 90–210 W and frequency in the range of 20–60 kHz. The desired operating frequency (i.e. 20, 45 and 60 kHz) can be selected through a selector switch on the panel in each experiment. Also, the desired ultrasound power (i.e. 90, 120, 150, 180 and 210 W) can be regulated by varying input AC voltage through an auto-transformer. When extraction experiments finished, the mixtures were withdrawn at regular intervals and filtered through a membrane filter for High Pressure Liquid Chromatography (HPLC) analysis. The effects of ethanol concentration from 50% to 80%, particle size from 0.095 mm to 0.995 mm, solvent to solid ratio varied from 10 ml to 60 ml/g, ultrasonic power of 90–210 W and ultrasonic frequency of 20–60 kHz on the extraction of flavonoids have been studied. To keep the temperature of the mixture constant, the extraction flask was maintained in the range of 25–70 °C by using a water bath around the flask. In the present study, all extraction experiments were carried out and analyzed in triplicate.

2.2. Extraction methods

2.2.1. Ultrasound-assisted extraction (UAE)

For ultrasound extraction, 5.0 g of sample powder of peanut shells and the predetermined volume of extracting solvent were put into a conical flask, in which the ratios of solvent and sample powder were fixed at 10, 15, 30, 40 and 60 ml/g. The mixture was irradiated for 80 min by placing into an ultrasound bath (300 × 240 × 150 mm) with ultrasonic power in the range of 90–210 W and frequency in the range of 20–60 kHz. The desired operating frequency (i.e. 20, 45 and 60 kHz) can be selected through a selector switch on the panel in each experiment. Also, the desired ultrasound power (i.e. 90, 120, 150, 180 and 210 W) can be regulated by varying input AC voltage through an auto-transformer. When extraction experiments finished, the mixtures were withdrawn at regular intervals and filtered through a membrane filter for High Pressure Liquid Chromatography (HPLC) analysis. The effects of ethanol concentration from 50% to 80%, particle size from 0.095 mm to 0.995 mm, solvent to solid ratio varied from 10 ml to 60 ml/g, ultrasonic power of 90–210 W and ultrasonic frequency of 20–60 kHz on the extraction of flavonoids have been studied. To keep the temperature of the mixture constant, the extraction flask was maintained in the range of 25–70 °C by using a water bath around the flask. In the present study, all extraction experiments were carried out and analyzed in triplicate.

2.2.2. Soxhlet extraction (SE)

In the present work, extraction experiments were performed in a classical Soxhlet apparatus which is composed of the condenser, thimble holder and distillation flask. During extraction process, ethanol of 150 ml was used as a solvent and 3.0 g powder of peanut shell sample was put into the thimble. Soxhlet extraction was performed at a high temperature of 98 °C for 320 min. After extraction, the mixtures were withdrawn at regular intervals, then filtered using a membrane filter. The concentration of sample was analyzed and determined using HPLC.

2.2.3. Heat-reflux extraction (HRE)

To further evaluate the efficacy of ultrasound-assisted extraction, heat-reflux extraction, another conventional extraction method, was performed at a temperature of 85 °C for 320 min. In the experiment, 3.0 g of sample powder of peanut shell was weighed and added into a flat bottom flask with 150 ml of 70% ethanol aqueous solution, the flask was immersed in a temperature-controlled water-bath shaker with a propeller for agitation and stirred at a speed of 200 rpm. The extracts were withdrawn at regular intervals and filtered by a membrane filter, and then analyzed by HPLC. The final extraction experiment at the
optimized variables was performed to compare it with UAE.

2.3. Determination of concentration of flavonoids

The extraction concentration of flavonoids was determined by using a aluminum nitrate colorimetric method reported by Bi et al [34]. 0.5 ml of the diluted sample solutions mixed with 70% ethanol aqueous solution to 5 ml was introduced to a 30 ml test tube, and then 0.3 ml NaNO₂ solution (5%) was added. About six minutes later, 0.3 ml AlCl₃ solution (10%) was also added. After another six minutes, 4 ml NaOH solution (1 mol/l) were added. The solution was homogeneously mixed and kept for 15 min at room temperature. Then by using the UV–Vis spectrophotometer, the absorbance at 510 nm was determined for the same mixture (no sample) as a blank. The extraction concentration of flavonoids was expressed as rutin with different concentrations through curve: $y = 0.9577x + 0.0084$ ($R^2 = 0.996$), where $x$ and $y$ are the concentration of flavonoids (mg/g) and the absorbance value of sample at 510 nm, respectively.

2.4. Mathematical models

Mathematical modelling can provide useful information for scale up of the extraction system and/or process, as well as help researchers and designers obtain the most effective process conditions and the excellent design parameters for optimizing purposes. Various mathematical models, such as first-order kinetic model [33], second-order kinetic model [32], Weibull model [35], two-site kinetic model [36], phenomenological model [28] and Peleg’s model [29,37] applied for describing UAE of active ingredients from plant products have been reported. Phenomenological model and Peleg’s model have been verified as the best describing models for assayed extractions due to their higher goodness of fit [38]. Similar results have been reported for the extraction of polyphenols from defatted fresh and distilled grape marc [39], ursolic acid from Ocimum sanctum by ultrasound [29] and bioactive compounds from dedo de moça pepper [40]. Hence both models could be applied for achieving good estimation of the extraction process of flavonoids from peanut shells under the studied range of various operating parameters.

2.4.1. Phenomenological mode

This model is composed of two main steps which are washing process (dissolution of the natural compounds located on the plant particles corresponding to a quickly released fraction $F$ at a fast rate defined by the rate constant of $K_1$) and slow extraction process (mass transfer of natural compounds through the solid plant particles into the bulk of the solvent by diffusion process corresponding to a slowly released part $1-F$ removed by a slower rate defined by the rate constant $K_2$) [28,38]. Both steps were here assumed to describe the kinetics of extraction of natural products and expressed by the following equation:

$$C_t = C_{eq} \times (1 - F \times \exp(-K_1 \times t) - (1 - F) \times \exp(-K_2 \times t))$$

where $t$ is the extraction time (min), $C_t$ is the concentration of flavonoids at $t$ (mg/g), $C_{eq}$ is the equilibrium solute concentration of flavonoids at saturation (mg/g), $K_1$ is the rate constant for washing (min⁻¹) and $K_2$ is the rate constant for diffusion (min⁻¹). $F$ and $1-F$ are the fraction of the solute released quickly and slowly (min⁻¹) respectively. The same model has been previously developed for modelling the kinetics of the extraction of resinoid from white lady’s bedstraw [41], as well as essential oils from hydrodistillation [28]. The coefficient of equation (1) was estimated by the multiple nonlinear regression method using all experimental values of the concentration of flavonoids.

2.4.2. Peleg’s model

Peleg’s model, a well-known semi-empirical kinetic model first proposed by Peleg in 1988 [42], was widely used because of its high performance to explain the extraction curves of active ingredients from plant materials [43-45]. In the present work, this model has also been applied for estimating the equilibrium concentration, initial extraction rate and rate constants. The model equation introduced by Peleg was adopted for the extraction of plant materials and shown below:

$$C_t = C_0 + \frac{t}{k_1 + k_2 t}$$

where $t$ is the extraction time (min), $C_t$ is the concentration of flavonoids at $t$ (mg/g), $C_0$ is the initial concentration of flavonoids, $k_1$ and $k_2$ are Peleg’s the rate constant (min g/mg) and capacity constant (g/mg) respectively. $C_0$ term can be omitted from equation (2) when initial concentration of flavonoids is zero in fresh solvent used at beginning. The extraction occurs at the first order trend in the very beginning stage and zero order in the latter stage respectively. The concentration of flavonoids was measured at corresponding time, the modified Peleg’s equation which explains the behavior of extraction process can be shown as follows:

$$C_t = \frac{t}{k_1 + k_2 t}$$

$C_t$ can be calculated by determining the Peleg’s constants ($k_1$ and $k_2$) from above mentioned equation (3) through depicting the curve between $1/C_t$ vs. $1/t$.

2.5. Statistical analysis

The experimental data were analyzed by Statistica 8.0 from Stat Soft Inc. (USA). Quasi-Newton method with non-linear regression was used to determine the parameters of two mentioned models from the experimental data. The performances of models were statistically measured by the coefficient of determination ($R^2$), the mean absolute errors (MPE) and/or the root mean squared deviation (RMSD).

3. Results and discussion

3.1. Optimization of different operating parameters and validation of model

In order to determine the optimal extraction time, the extraction experiments with different ethanol concentration have been carried out. The results obtained for the variation in the amount of flavonoids extracted per g of peanut shells with time have been depicted in Fig. 1.

It can be seen that the extraction of flavonoids was very fast during the first 20 min with extraction time. Hereafter, the flavonoids concentration increased gradually with time till 80 min. According to the above observation, extraction time of 80 min gave the maximum release of flavonoids from peanut shells in the case of ultrasound-assisted extraction. Therefore, in the present work, all the experiments on the effects of operating parameters on the extraction of flavonoids were carried out for 80 min.

3.1.1. Effect of ethanol concentration on extraction of flavonoids

Generally, water is not a preferred solvent for the extraction of flavonoids, but studies have shown that a small amount of water added to the extraction solvent is favorable for promoting the increase of the extraction yield of target compounds. In the present work, the mixtures of ethanol–water were selected as extraction solvent. To first determine the best concentration of aqueous ethanol for the following studies, four different ethanol concentrations of 50%, 60%, 70% and 80% were used to understand the effect of extracting flavonoids from peanut shells. The constant extraction conditions were fixed as follows: raw material particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic power of 120 W, ultrasonic frequency of 45 kHz and extraction time of 80 min. The results shown in Fig. 1 clearly observed that the extraction of flavonoids from peanut shells was
concentration of 70%. When the solvent concentration of ethanol was
obtained from phenomenological model constants viz. the fraction of the
solute released quickly of
obtained in ethanol concentration of 70%, it was used as the most
suitable solvent concentration for extraction of flavonoids from peanut
shells. Considering these facts, particle size of 0.285 mm used in this study was
considered the most suitable for the extraction of flavonoids from peanut
shells.

To validate the phenomenological model, the extraction curves ob-
tained from phenomenological model constants viz. the fraction of the
solvent released quickly of F, the rate constant for washing of K₁ (min⁻¹)
and the rate constant for diffusion of K₂ (min⁻¹) and their comparison
with the experimental data were also plotted in Fig. 1. It was clearly
found that there was a satisfactory agreement between experimental and
predicted values of the concentration of flavonoids. All experimental
errors within ±3% of the mean reported values were also found, which
indicated that phenomenological model has good fitting accuracy. The
calculated phenomenological model constants and the root mean
squared deviation (RMSD) for extraction of flavonoids at different
ethanol concentrations have been summarized in Table 1.

3.1.2. Effect of particle size on extraction of flavonoids

It is known that particle size plays an important role in the extraction
of target compounds from natural products. To investigate the influence of particle size on the yield of flavonoids from peanut shells, The particle
sizes used in this work was 0.095, 0.285, 0.365, 0.675 and 0.995 mm,
respectively. Extraction experiments were performed with ethanol
concentration of 70%, solvent to solid ratio of 40 ml/g, extraction
temperature of 55 °C, ultrasonic power of 120 W, ultrasonic frequency of
45 kHz and extraction time of 80 min. The obtained results have been
given in Fig. 2.

It can be seen that the yields of flavonoids increased gradually with a
reduction in particle size between 0.995 and 0.365 mm and the maximum extraction yield appeared at particle size of 0.285 mm. This
phenomena was probably linked to the fact that larger particle decrease
the interfacial area so that diffusion paths were shorten in the solid
matrix, which might be easy to decrease with the increase of size for the
yield at a given time. However, when the particle size decreased to
0.095 mm, the yield of flavonoids decreased slightly. diffusion might not
play a significant role in the extraction of such small particle. Thus, a
further decrease in the size might not cause a corresponding increase in
the yield of flavonoids. Similar results have been reported [46,47].

Considering these facts, particle size of 0.285 mm used in this study was
considered the most suitable for the extraction of flavonoids from peanut
shells.

Table 1

| Solvent concentration (%) | Cexp (mg/g) | Ccal (mg/g) | F | K₁ (min⁻¹) | K₂ (min⁻¹) | RMSE |
|---------------------------|------------|------------|---|------------|------------|------|
| 50                        | 7.991      | 7.597      | 0.423 | 2.270 | 0.139 | 0.323 |
| 60                        | 8.855      | 8.620      | 0.561 | 5.625 | 0.244 | 0.251 |
| 70                        | 9.263      | 9.198      | 0.685 | 6.483 | 0.433 | 0.126 |
| 80                        | 7.163      | 6.980      | 0.724 | 7.309 | 0.547 | 0.108 |

Fig. 1. Effect of different ethanol concentrations on the extraction of flavonoids from peanut shells and phenomenological model fitting (particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic power of 120 W, ultrasonic frequency of 45 kHz and extraction time of 80 min).
efficiency, the effect of solvent to solid ratio in the range of 10–60 ml/g on extraction of flavonoids was investigated by using 70% ethanol as the solvent for 80 min, and other operating parameters including particle size of 0.285 mm, extraction temperature of 55 °C, ultrasonic power of 120 W and ultrasonic frequency of 45 kHz.

As shown in Fig. 3, the extraction yield of flavonoids increased gradually from 7.516 to almost 9.263 mg/g when the solvent to solid ratio was increased from 10 to 40 ml/g. However, when the solvent to solid ratio was further increased up to 60 ml/g, the extraction yield of flavonoids prominently reduced to 6.128 mg/g. The reason for the above phenomena is probably that ultrasonic wave is able to prompt the establishment of equilibrium for dissolution of the target compounds between solvent and the plant cells. Additionally, effective swelling of the solid material can be happened through increasing in the amount of ethanol and the surface area for solute solvent contact. Generally, the

Table 2

| Particle size (mm) | $C_{eq}$ (mg/g) | $F$ | $K_1$ (min$^{-1}$) | $K_2$ (min$^{-1}$) | RMSE |
|-------------------|----------------|-----|-------------------|-------------------|------|
| 0.095             | 8.305          | 8.236 | 0.538            | 3.665             | 0.324 |
| 0.285             | 9.263          | 9.198 | 0.685            | 6.483             | 0.433 |
| 0.365             | 7.906          | 7.754 | 0.625            | 6.883             | 0.521 |
| 0.675             | 7.385          | 7.406 | 0.771            | 7.154             | 0.665 |
| 0.995             | 6.898          | 6.755 | 0.652            | 7.006             | 0.678 |

Fig. 2. Effect of different particle sizes on the extraction of flavonoids from peanut shells and phenomenological model fitting (70% ethanol as the solvent, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic power of 120 W, ultrasonic frequency of 45 kHz and extraction time of 80 min).

Fig. 3. Effect of different solvent to solid ratios on extraction of flavonoids from peanut shells and phenomenological model fitting (70% ethanol as the solvent, particle size of 0.285 mm, extraction temperature of 55 °C, ultrasonic power of 120 W, ultrasonic frequency of 45 kHz and extraction time of 80 min).
dilute effect of solvent is more when the more quantity of solvent are used for a fixed amount of solid material, thus a faster extraction efficiency will be occurred due to a larger concentration difference between the external solvent and the interior of the plant cells. But if the extra solvent further increases and the solution is too dilute, the concentration difference will not be a sufficient increase, thus the increase in extraction yield will be limited [48,49]. Therefore, as shown in Fig. 3, the extraction yield of flavonoids did not increase but decreased significantly when the solvent to solid ratio increased from 40 to 60 mL/g. Hence, the solvent to solid ratio of 40 mL/g was taken as the optimal ratio in the extraction of flavonoids and used for the subsequent experiments.

The concentration values of flavonoids were modeled and fitted in the phenomenological model at different times for different solvent to solid ratios in Fig. 3, which showed a good agreement between experimental and predicted values. The calculated parameters of phenomenological model and \( C_{eq} \) for flavonoids extraction for different solvent to solid ratios have been also given in Table 3.

### 3.1.4. Effect of extraction temperature on extraction of flavonoids

Extraction temperature also plays an important role in the extraction of compounds from raw materials. To investigate the influence of extraction temperature on the extraction efficiency, experiments were carried out at four different temperatures viz. 25, 40, 55 and 70 ℃. Other conditions were fixed as follows: ethanol of 70%, solvent to solid ratio of 40 mL/g, material particle size of 0.285 mm, ultrasonic power of 250 W and ultrasonic frequency of 22 kHz and extraction time of 80 min. The experimental results were shown in Fig. 4.

It can be seen from the figure that the concentration of flavonoids increased progressively with the increase in extraction temperature from 25 to 55 ℃ and reached a maximum at 55 ℃. One possible reason might be an increase in solubility of flavonoids with the increase in mass transfer as well as a reduction in solvent viscosity. Moreover, the increase observed in the extraction yields of flavonoids might be linked to the fact that the higher temperature would lead to the diffusivity increase and solvent viscosity decrease, thus increase in the extraction temperature giving a corresponding increase in the efficiency of extraction [50]. When over 55 ℃, however, the yield of flavonoids decreased slightly. This may be ascribed to the fact that higher temperature is not favorable for the extraction of flavonoids due to evaporation of ethanol solvent. Furthermore, the degradation of flavonoids caused by high temperature is another important reason for the decrease of extraction yield of flavonoids [51]. Based on the above results, also considering for too high temperature may lead to the increase of energy cost. Therefore, the extraction temperature of 55 ℃ was selected as the optimum temperature for the following experiments.

Fig. 4 also plotted the extraction curves according to phenomenological model constants. Comparison between the experimental and calculated values of concentration of flavonoids in extract has been done. It can be observed that there was a good agreement between the experimental and calculated values. The validity of the phenomenological model also can be observed by the values of RMSE which have been summarized in Table 4.

### 3.1.5. Effect of ultrasonic power on extraction of flavonoids

The effect of ultrasound power on the extraction of flavonoids from peanut shells was studied at five different ultrasound powers (i.e. 90, 120, 150, 180 and 210 W) under extraction conditions of solvent as 70% ethanol, particle size of 285 mm and ultrasonic frequency of 45 kHz at temperature of 55 ℃ after 80 min of ultrasonic treatment. As shown in Fig. 5, the extraction of flavonoids increased prominently with the increase in ultrasonic power from 90 to 120 W, then there was a slight increase in ultrasonic power rising from 120 to 150 W. However, when the ultrasonic power was further increased up to 210 W, the extraction yield of flavonoids decreased slightly. The results might be likely attributed to the fact that ultrasonic power with larger amplitude travelled through the ethanol solvent resulting in intense collapse of cavities, which would cause the increase of many physical effects including increased solute diffusion, local energy dissipation, cracked or damaged cell wall and interfacial turbulence. These physical effects were expected to enhance the extraction yield of flavonoids at higher ultrasonic power [52]. The slight increase of the extraction yield at ultrasonic power of 150 W might depend on the combination of reduction of the cavitation effect and the absorption of heat. Additionally, beyond ultrasonic power of 150 W resulted in a slight reduction in the extraction due to degradation of flavonoids [53]. Therefore, Considering green extraction with lower energy consumption and commercial application, ultrasonic power of 120 W was selected the most suitable ultrasound power for the extraction of flavonoids.

The concentration values of flavonoids were modeled and fitted in the phenomenological model at different times for different ultrasonic powers in Fig. 5, which showed a good agreement between experimental and predicted values. The calculated parameters of phenomenological model and \( C_{eq} \) for the extraction of flavonoids at different ultrasonic powers have been also given in Table 5.

### 3.1.6. Effect of ultrasonic frequency on extraction of flavonoids

There is limited study for the effect of ultrasonic frequency on the extraction of flavonoids. Thus, in the present work, ultrasonic frequency at different levels viz. 20, 45 and 60 kHz was investigated under the optimal extraction parameters determined earlier. The results have been shown in Fig. 6 and it was observed that the extraction yield of flavonoids increased significantly with the increase of ultrasonic frequency from 20 to 45 kHz and reached the highest value of 9.263 mg/g at 45 kHz. One possible reason was that higher ultrasonic frequency corresponding to higher energy dissipation which resulted in the increased mass transfer. Moreover, the increased extraction yield might be explain from the viewpoint of energy efficiency of sonochemical processes. Higher frequency was favorable because the cavity reduced to a smaller size, so that the collapse was more violent. The similar effects of ultrasonic frequency on the extraction of glycyrrhizic acid from the root of licorice [54] and salvianolic acid B from Salvia miltiorrhiza root [55] were previously reported. However, it was also found that a decrease in the extraction yield was significant when ultrasonic frequency further increased to 60 kHz. The reason for this phenomena was probably that too high frequency would lead to the cavitation bubbles swelling time shorter and has no time to collapse, which would reduce the cumulative effects of cavitation at the same intensity of irradiation [56]. Similar results of decrease in the extraction of active ingredients from natural products with higher frequency have been reported [57,58]. Consequently, it was expected to understand that the optimal ultrasonic frequency of 45 kHz with a better effect on the extraction of flavonoids from peanut shells could attract higher extraction efficiency.

The values of flavonoids concentration from peanut shells at different time for different ultrasonic frequencies were predicted from phenomenological model and depicted in Fig. 6 and Table 6 respectively, which showed a good agreement with a slight lost of goodness of fit based on RMSE between the experimental values and the predicted
3.2. Comparison of ultrasound-assisted extraction with other extraction methods

The extraction of flavonoids from peanut shells using ultrasound-assisted extraction, Soxhlet extraction and heat reflux extraction was compared and shown in Fig. 7.

It could be found that 9.263 mg/g of flavonoids was obtained by ultrasound-assisted extraction approach which was significantly higher than that of 5.581 mg/g obtained by heat reflux extraction. It also could be seen from this figure that the time required by ultrasound-assisted extraction was only 80 min as compared to 320 min that of heat reflux extraction at high temperature. Additionally, the extraction result by using Soxhlet extraction though was approximately equal to that of

Table 4

| Temperature (°C) | Ceq (mg/g) | F | K₁ (min⁻¹) | K₂ (min⁻¹) | RMSE Exp. | RMSE Cal. |
|-----------------|------------|---|-------------|-------------|----------|-----------|
| 25              | 7.552      | 7.363 | 0.598 | 4.218 | 0.325 | 0.239 |
| 40              | 8.105      | 8.096 | 0.654 | 5.651 | 0.420 | 0.223 |
| 55              | 9.263      | 9.198 | 0.685 | 6.483 | 0.433 | 0.126 |
| 70              | 8.995      | 9.053 | 0.720 | 6.987 | 0.521 | 0.108 |

values of phenomenological model.
ultrasound-assisted extraction, it was performed at much higher temperature of 98 °C and for very long time of 320 min as compared to ultrasound assisted extraction at temperature of 55 °C for time of 80 min only. Therefore, the comparison results of these three extraction methods indicated that ultrasound-assisted extraction was a more effective method than other two extraction methods. This higher efficiency of ultrasound-assisted extraction was more likely to the reason that the shock waves and shear forces generated by cavitation, which could promote the release of targeted compounds due to the physical disruption of tissues and plant cell wall, was favorable for enhancement in the ultrasonic extraction process [26]. Meanwhile, ultrasonic wave was beneficial to improve mass transfer, as well as to cause a greater contact area between solid and liquid phase leading to the presence of more efficient solvent penetration to plant cell [59]. Thereby, the best advantage of ultrasonic extraction method was the lower operation temperature and the significant reduction in the treatment time compared to other methods.

3.3. Comparison and analysis of extraction models

In order to evaluate the most appropriate model for characterizing the behavior of solid–liquid extraction of flavonoids from peanut shells, the present work introduced the comparison of two well-known models viz. phenomenological model and Peleg’s model to explain extraction kinetic of flavonoids. The mean absolute errors (MPE) between experimental data and model predictions were used to evaluate the performance of models and their comparisons due to the effectiveness of MPE according to the previous literature [60]. The calculated parameters of phenomenological model (i.e. constants \( F, K_1 \) (min\(^{-1}\)) and \( K_2 \) (min\(^{-1}\)) of phenomenological model for extraction of flavonoids from peanut shells (ethanol concentration of 70%, particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic frequency of 45 kHz and extraction time of 80 min).

### Table 5

| Ultrasonic power (W) | \( C_{eq} \) (mg/g) Exp. | \( C_{eq} \) (mg/g) Cal. | \( F \) | \( K_1 \) (min\(^{-1}\)) | \( K_2 \) (min\(^{-1}\)) | RMSE |
|----------------------|-------------------------|-------------------------|--------|-------------------------|-------------------------|------|
| 90                   | 6.521                   | 6.754                   | 0.571  | 5.879                   | 0.399                   | 0.314|
| 120                  | 9.205                   | 9.213                   | 0.664  | 6.578                   | 0.521                   | 0.117|
| 150                  | 9.263                   | 9.198                   | 0.685  | 6.483                   | 0.433                   | 0.126|
| 180                  | 8.108                   | 8.228                   | 0.724  | 5.689                   | 0.569                   | 0.218|
| 210                  | 8.468                   | 8.532                   | 0.598  | 6.025                   | 0.461                   | 0.225|

Fig. 6. Effect of different ultrasonic frequencies on extraction of flavonoids from peanut shells and phenomenological model fitting (70% ethanol as the solvent, particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperature of 55 °C, ultrasonic power of 120 W and extraction time of 80 min).

### Table 6

| Ultrasonic frequency (kHz) | \( C_{eq} \) (mg/g) Exp. | \( C_{eq} \) (mg/g) Cal. | \( F \) | \( K_1 \) (min\(^{-1}\)) | \( K_2 \) (min\(^{-1}\)) | RMSE |
|---------------------------|-------------------------|-------------------------|--------|-------------------------|-------------------------|------|
| 20                        | 5.961                   | 5.880                   | 0.529  | 5.136                   | 0.423                   | 0.230|
| 45                        | 9.263                   | 9.198                   | 0.685  | 6.483                   | 0.433                   | 0.126|
| 60                        | 6.579                   | 6.445                   | 0.649  | 6.997                   | 0.501                   | 0.206|

Fig. 7. Comparison of Soxhlet extraction at temperature of 98 °C for 320 min, heat reflux extraction at temperature of 85 °C for 320 min and ultrasound-assisted extraction at temperature of 55 °C for 80 min (70% ethanol as the solvent, particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, ultrasonic power of 120 W and ultrasonic frequency of 45 kHz).
determined by adapting phenomenological model (Eq. (1)) and Peleg’s model (Eq. (3)), as well as adapting experimental data obtained from the extraction of flavonoids under the influences of ethanol concentration and extraction temperature. The results of analyses were given in Table 7.

It could be observed that the MPE of phenomenological model varied in a low range of 0.158%–0.809% with the change of ethanol concentration and temperature, as well Peleg’s model were found to be well to describe the extraction processes due to the low MPE from 0.675 to 1.817% according to the results in Table 7. The theoretical extraction curves of flavonoids have been plotted by using the phenomenological model which exhibited high consistency with the experimental data at all studied conditions according to Fig. 8.

Higher goodness of fit in Fig. 8 suggested that the extraction process of flavonoids from peanut shells could be adequately described by phenomenological model. The results also verified phenomenological model equation to be a best describing model for the behavior of solid–liquid extraction of flavonoids. Success of phenomenological model for fitting of experimental data may benefit from its two term groups viz. the fast released fraction and the slow released fraction in the extraction process, so that to make it superior than Peleg’s model [38].

Phenomenological model though was concluded as the best equation describing the behavior of flavonoids extraction process owing to the lower MPE value, Peleg’s model also displayed a good performance with a slight loss of goodness of fit in Fig. 8 compared with phenomenological model. Moreover, Peleg’s model equation including only two terms was its another superiority, whereas Phenomenological model equation involving four terms which made it more complicated compared with Peleg’s model. Therefore, based on the above results and analysis, both models could be used to get good estimation of the solid–liquid extraction of flavonoids from peanut shells under the studied range of ethanol concentration and extraction temperature.

4. Conclusion

This work focused on the process optimization for understanding the influences of different operating parameters on the extraction of flavonoids from peanut shells under ultrasound irradiation. The important role of ultrasound-assisted extraction has been confirmed according to the comparative studies with the conventional extraction approaches such as Soxhlet extraction and heat reflux extraction. The obtained results in UAE was of lower extraction temperature, much shorter time and higher flavonoids yields than the conventional methods. The maximum extraction of flavonoids (9.263 mg/g) (70% ethanol as the solvent, particle size of 0.285 mm, solvent to solid ratio of 40 ml/g, extraction temperatures of 55 °C, ultrasonic power of 120 W and ultrasonic frequency of 45 kHz) was obtained in just 80 min, which showed that the ultrasound can be applied for improving the extraction efficiency and reducing the extraction time of flavonoids. Two kinetic model viz. phenomenological model and Peleg’s model have been used to elucidate the extraction kinetics and predict the amount of flavonoids at given time. In accordance with statistical indicators, both phenomenological model with a lower range MPE of 0.158–0.809% and Peleg’s model with the MPE from 0.675 to 1.817% showed a satisfactory agreement between experimental and predicted values of the flavonoids concentration, which may make the application of these two models for the purpose of optimization and modelling for the extraction process of flavonoids from peanut shells.

![Fig. 8. Comparison of phenomenological model and Peleg’s model fitting to experimental data obtained from the extraction of flavonoids under the effect of ethanol concentration (A) and extraction temperature (B).](image-url)

Table 7

Mean percent absolute errors of two extraction parameters (i.e. ethanol concentration and temperature) between experimental data and extraction model results.

| Ethanol concentration (%) | $C_{eq}$ (mg/g) Exp. | $C_{eq}$ (mg/g) Cal.$^a$ | $C_{eq}$ (mg/g) Cal.$^b$ | Phenomenological model | Peleg’s model |
|---------------------------|----------------------|----------------------------|---------------------------|------------------------|----------------|
|                           |                      | $K_1$ (min$^{-1}$)         | $K_2$ (min$^{-1}$)        | MPE (%)                | $k_1$ (min g/mg) | $k_2$ (g/mg) | MPE (%) |
| 50                        | 7.891                | 2.270                      | 0.139                     | 0.655                  | 0.155          | 0.112      | 1.047   |
| 70                        | 9.263                | 6.483                      | 0.433                     | 0.158                  | 0.163          | 0.215      | 0.675   |
| 80                        | 7.163                | 7.309                      | 0.547                     | 0.850                  | 0.234          | 0.548      | 1.045   |
| 55                        | 7.552                | 4.218                      | 0.325                     | 0.809                  | 0.205          | 0.197      | 0.996   |
| 70                        | 8.995                | 6.987                      | 0.521                     | 0.364                  | 0.369          | 0.288      | 1.817   |

$^a$ Calculated $C_{eq}$ of phenomenological model.

$^b$ Calculated $C_{eq}$ of Peleg’s model.
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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