A generalized energy-based kinetic model for microwave-assisted extraction of bioactive compounds from plants

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ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form 30 January 2015
Accepted 31 January 2015
Available online 7 February 2015

Keywords:
Absorbed power density (APD)
Absorbed energy density (AED)
Generalized model
Heating modes
Normalized extraction yield

ABSTRACT

By considering the absorbed power and energy based on heating power profile during extraction, a generalized model with washing coefficient (*b*), diffusion coefficient (*k*) and predictive parameter namely absorbed power density (APD) was developed for microwave-assisted extraction (MAE) at any operational heating modes. To study the model, MAE of flavonoids from cocoa (*Theobroma cacao* L.) leaves was conducted using the heating modes (constant-power, two-steps-power, intermittent-power and constant-temperature) at various microwave power (100–300 W) and extraction temperature (50 °C and 70 °C). The results shows that the model ($b = 0.5595$ and $k' = 0.01279$ mL/J) is able to predict the normalized extraction yields of MAE at any heating modes, heating power, microwave system, extraction scale and batch of plant sample with less than 4% discrepancy. The accuracy of the prediction relies on particle size of sample (0.25–0.60 mm), type of extraction solvent (85% aqueous ethanol) and solvent to feed ratio (50 mL/g).

1. Introduction

Microwave-assisted extraction (MAE) is an advanced extraction technique which employs microwave heating in an extraction system. MAE has been widely employed to extract valuable active compounds from plant materials [1,2] and plant-based waste residues [3,4]. In general, the performance of MAE depends on its operational mode of heating [5], e.g. constant-power heating, intermittent-power heating and constant-temperature heating. Constant-power MAE delivers persistent heating at specific power to extraction system and it is a known as the standard practice to extract thermally-stable active compounds [6]; intermittent-power MAE provides pulsed microwave heating at certain power which is efficient in extracting thermal-labile compounds [7] while constant temperature MAE controls extraction temperature which enables the extraction of highly degradable active compounds [8]. These heating modes are broadly adopted in MAE as far as plant extraction is concerned. Thus, their kinetic modeling would provide insightful information on the extraction behaviors to facilitate the optimization and scaling up operations.

Empirical model such as film theory, chemical kinetic equation and other two-parametric models has been conventionally used to model assisted extraction techniques including MAE [9]. These models can only indicate the extraction kinetics at specific operating conditions and extraction techniques as their extraction constants are obtained by curve-fitting through experimental data. Empirical models developed based on response surface methodology (RSM) and artificial neural network (ANN) had been applied to simulate and optimize the operating parameters of MAE [10,11]. These models require lesser experimental data for the simulation as compared to conventional empirical MAE model. However, screening of suitable range of operating parameters is essential to achieve reliable optimization results. Modeling of MAE had been attempted using transport equations such as Maxwell's, energy and species balance equations via COMSOL Multiphysics™ software [12]. Both the distribution of electromagnetic wave and temperature profile for constant-power and intermittent-power MAE can be simulated theoretically based on the model, whereas their extraction profiles can only be modeled based on experimentally-fitted empirical parameters [12]. All the models mentioned employ empirical approach to model the mass transport phenomenon of MAE process. They are applicable only at specific operating condition, heating mode and microwave system. To broaden the predictive capability of MAE model, two energy-related parameters namely absorbed power density (APD) and absorbed energy density (AED) had been introduced and were incorporated into conventional empirical model as parameters to predict the extraction profile of MAE at various microwave powers and extraction scales [13]. These energy-related parameters, i.e. APD and AED

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http://dx.doi.org/10.1016/j.seppur.2015.01.041
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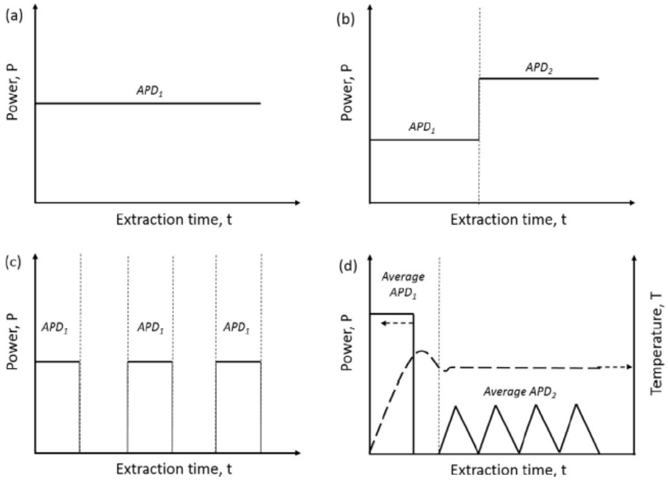

Fig. 1. Heating-power profiles of various operational modes of MAE: (a) constant power heating; (b) two-steps power heating; (c) intermittent power heating and (d) constant temperature heating.

Table 1
APD values of MAE systems.

Microwave system	Solvent loading, V (mL)	Microwave irradiation power, P (W)	Absorbed power density, APD (W/mL)
Samsung MW718	100	100	0.15 ± 0.02
		150	0.30 ± 0.03
		300	0.93 ± 0.06
Milestone RotoSYNTH	100	38	0.11 ± 0.03
		62	0.17 ± 0.02
		101	0.60 ± 0.02
		209	1.26 ± 0.05

MAE operating conditions	Heating time, t_H (min)	Total heat absorbed, Q (J)	Absorbed power density, APD (W/mL)	Average APD (W/mL)
Example of calculation of APD by calorimetric method				
100 mL, 100 W (Samsung MW718)	5.00	5266	0.18	0.15
	13.00	10,796	0.14	
	27.00	23,649	0.15	

are indicators for heating performance of MAE and the progress of the extraction to reach equilibrium state, respectively. Beside the involvement in modeling study, APD and AED can also be adopted in the optimization of MAE at various extraction scale [14]. This validated APD-AED predictive model is applicable only for constant-power MAE and its predictive capabilities in various heating modes and extraction system have yet to be confirmed.

In this study, the absorbed power and energy of a MAE system at each heating steps based on its heating-power profile was taken into account in the development of the generalized predictive model to study the MAE of flavonoids from cocoa (*Theobroma cacao* L.) leaves at constant power, two steps power, intermittent power and constant temperature heating. The capabilities of the model to predict the extraction profile of MAE were evaluated at various conditions such as at different heating power, heating modes and microwave system. This work also analyzes the intrinsic effects exerted by the APD and AED parameters on the extraction mechanism of MAE.

2. Materials and methods

2.1. Materials and reagents

Denatured alcohol was obtained from LGC Scientific co. (Malaysia) as extraction solvent. Standard of flavonoid compounds such as isoquercitrin, (−)-epicatechin and rutin were purchased from Sigma–Aldrich co. (USA). Acetonitrile and ethanol are purchased from Merck co. (Germany) as mobile phase for chromatography analysis.

2.2. Sample preparation

Fresh cocoa leaves collected from local cocoa plantation were dried using conventional air-drying oven at 40 °C for a day. The dried leaves (5–6% moisture content) were then cut and powdered to 0.25–0.60 mm particle size and stored at 4 °C in a container.

2.3. Microwave-assisted extraction at various heating modes

Two (2) g of cocoa leaves sample was mixed with 100 mL of 85% (v/v) aqueous ethanol (optimum solvent) in a 500 mL closed Duran bottle. The mixture was put inside a microwave system and heated up using predetermined operating conditions based on certain heating-power profile as shown in Fig. 1. In this study, domestic microwave oven (Samsung MW718) was employed to perform constant-power, two-steps-power and intermittent-power MAE at various microwave power ranging from 100 to 300 W. In constant-power MAE, the extraction mixture was heated up using fixed power without stirring; two-steps power MAE involved sequential heating using two power levels and the intermittent-power MAE provided pulsed heating at fixed power. The latter heating mode was adjusted by turning on and off the microwave system based on intermittency ratio, $\alpha = \tau_{on}/(\tau_{on} + \tau_{on})$ [7], where τ_{on} and τ_{off} are the respective on and off periods (min) of each cycle (one on plus one off periods). On the other hand, temperature-controlled microwave system (Milestone RotoSYNTH) was used to carry out constant-temperature MAE at 50 °C and 70 °C. In this MAE, microwave power of 500 W was applied to ramp up the extraction temperature to the desired set point. After the desired

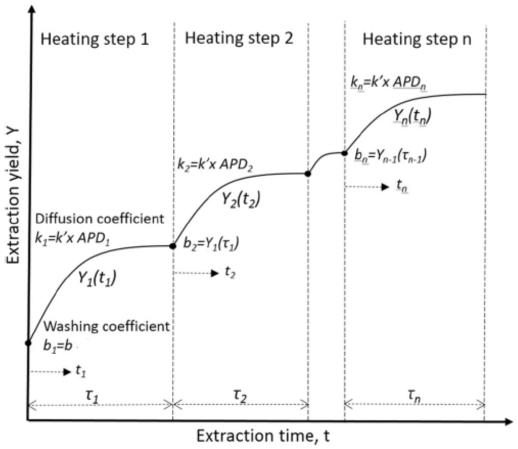

Fig. 2. Schematic diagram of the development of generalized predictive film theory-APD model.

temperature was reached, the extraction temperature was maintained by regulating the nominal microwave power. Upon subjected to certain mode of heating, the extraction mixture was cooled down to room temperature using a water bath. The extract was filtered using fine cloth followed by 0.2 μm regenerated cellulose filter prior to HPLC analysis. To construct an extraction profile of MAE, extractions at predetermined operating conditions were conducted at varying extraction times using fresh samples. Since the overall extraction trend is far more important than the accuracy of each extraction point in this modeling study, replication of the experiment in this case is not necessarily as it only indicates the reproducibility of extraction yield at each extraction points.

2.4. Quantification of flavonoids in cocoa leaves extract

High performance liquid chromatography (HPLC) was performed to quantify three flavonoid compounds from cocoa leaves extract. Agilent 1200 Series HPLC device with Agilent ZORBAX Eclipse Plus C18 column, 5 μm (4.6 mm × 150 mm) configured with Bonaccorsi et al. method [15] was employed in this analysis. The flavonoids was analyzed at 350 nm for isoquercitrin and rutin compounds and 280 nm for (−)-epicatechin compound using UV-DAD detector. Mobile phase used in this analysis consists of linear gradient of acetonitrile in water: 5–20% (0–15 min), 20–30% (15–20 min), 30–50% (20–30 min), 50–100% (30–35 min), 100% (35–40 min), and 100–5% (40–50 min) at flow rate of 1.0 mL/min. The extraction yield is expressed as the mass of extracted active compounds (mg) per mass of sample used (g). The total extraction yields of isoquercitrin, (−)-epicatechin and rutin were the response of the modeling study.

2.5. Determination of energy-related parameters

The proposed model relies on values of absorbed power density (APD) and absorbed energy density (AED) of the MAE system at various heating powers. APD and AED represent the absorbed microwave power (W/mL) and absorbed microwave energy (J/mL) per unit solvent volume, respectively. The detail procedure for the determination of APD and AED was reported in the previous work [13]. APD can be determined experimentally by measuring the absorbed power of a blank extraction solvent heated using a specific nominal microwave power based on Eq. (1).

$$\mathrm{APD} = \frac{Q}{V \cdot t_H} \tag{1}$$

where Q is the total energy absorbed by solvent during heating (J), V is the solvent volume (mL) and t_H is the heating time (min). The total heat absorbed, Q can be calculated from the evolved temperature profile based on heat capacity of the solvent. In this study, a representative value of APD of blank extraction solvent under various nominal microwave power were determined by averaging the APD values calculated for each conditions at different heating time (t_H). Due to fluctuation in microwave irradiation power during constant-temperature MAE, the APD values were determined based on two average microwave powers, i.e. the power to ramp the extraction temperature to desired set point and the power to maintain the desired temperature across the time as indicated in Fig. 1. The calculated average APD values of MAE systems are tabulated in Table 1. The energy-related parameter, AED is related to APD and the extraction time via Eq. (2).

$$\mathrm{AED}_t = \mathrm{APD} \times t \tag{2}$$

where AED_t is the total microwave energy absorbed per solvent volume during the extraction (J/mL) and t is the extraction time (min).

2.6. Generalized energy-based MAE model

The typical extraction profile, i.e. yield vs. time of MAE consists of two stages. The first stage involves the washing of active compounds from the broken plant cells by the bulk solvent in a fast rate due to sample preparation e.g. grinding and in the second stage, the diffusion of active compounds from the microwave-ruptured cells into the bulk solvent. This study focuses only on the diffusion stage as this stage is strongly influenced by the operating conditions of MAE. Film theory model [16] as expressed in Eq. (3) is suitable to model the normalized extraction yield of the diffusion stage.

2.6.1. Film theory model

$$Y = \frac{y}{y_s} = 1 - (1 - b)\exp(-k \cdot t) \tag{3}$$

where Y is the normalized extraction yield, y is the extraction yield (mg/g), y_s is the equilibrium extraction yield (mg/g), b and k indicate the extraction kinetics for the washing (1) and diffusion (min^{-1}) stages, respectively. By adapting Eq. (3) with AED as a basis to replace the extraction time t, a simple energy-based model can be developed to simulate the progress of a MAE to reach equilibrium extraction stage based on the amount of microwave energy absorbed in the system as follows:

2.6.2. AED-film theory model

$$Y = \frac{y}{y_s} = 1 - (1 - b)\exp(-k' \cdot \mathrm{AED}_t) \tag{4}$$

where k' is the kinetic constants for the diffusion stage in energy basis (mL/J). The simulated energy-based extraction profile, i.e. normalized yield vs. AED is generally applicable over constant-power MAE operated at any heating conditions [13]. This model can be rewritten in Eq. (5) to predict the normalized extraction profile in time basis based on the actual heating power of the MAE system (APD value).

Table 2
Experimental design for extraction curves of MAE.

No.	Heating modes	Heating conditions	Equilibrium extraction yields (mg/g)			Total equilibrium extraction yield (mg/g)
			IQ	EC	RT	
1	Constant power	Samsung MW718; 150 W, 20 min	2.35 ± 0.02	2.59 ± 0.03	4.89 ± 0.06	9.82 ± 0.07
2	Two-steps power	Samsung MW718; step 1: 100 W, 13.46 min; step 2: 300 W, 4.14 min	2.55 ± 0.01	2.80 ± 0.01	5.15 ± 0.05	10.50 ± 0.05
3		Samsung MW718; step 1: 300 W, 3.20 min; step 2: 100 W, 6.40 min	2.62 ± 0.02	2.76 ± 0.07	5.27 ± 0.03	10.65 ± 0.12
4	Intermittent power	Samsung MW718; 150 W, $\alpha = 0.50$ (on: 4 min, off: 4 min) for 32 min	2.31 ± 0.09	2.49 ± 0.01	5.08 ± 0.02	9.89 ± 0.11
5		Samsung MW718; 300 W, $\alpha = 0.25$ (on: 1 min, off: 3 min) for 16 min	2.38 ± 0.01	2.52 ± 0.03	5.02 ± 0.05	9.93 ± 0.10
6	Constant temperature	Milestone RotoSYNTH; 500 W (ramping for 25 s), 50 °C, 30 min	2.04 ± 0.09	2.66 ± 0.07	5.10 ± 0.02	9.79 ± 0.06
7		Milestone RotoSYNTH; 500 W (ramping for 40 s), 70 °C, 15 min	2.20 ± 0.04	2.67 ± 0.11	5.13 ± 0.06	10.00 ± 0.18

2.6.3. Predictive AED-film theory model

$$Y = \frac{y}{y_s} = 1 - (1 - b)\exp(-k' \cdot \mathrm{APD} \cdot t) \qquad (5)$$

To extend the applicability of this model to two-steps-power, intermittent-power and constant-temperature MAE, the APD values of each heating steps involved in the MAE were incorporated into the model as illustrated in Fig. 2. As a result, a generalized energy-based MAE model was proposed to describe the normalized extraction yield of MAE at ith heating step, Y_i as shown in Eq. (6)

2.6.4. Generalized predictive AED-film theory model

$$Y_i(t) = \frac{y}{y_s} = 1 - (1 - b_i)\exp\left[-k_i \cdot \left(t - \sum_{j=0}^{i-1} \tau_j\right)\right] \qquad (6)$$

where τ is the total time period in a heating step, b_i and k_i are the washing and diffusion coefficient at ith heating step, respectively. The individual washing and diffusion coefficients involved in each heating steps can respectively be calculated using Eqs. (7) and (8):

$$\begin{aligned} b_i &= Y_{i-1}(\tau_{i-1}) \\ &= 1 - (1 - b_{i-1})\exp(-k' \cdot \mathrm{APD}_{i-1} \cdot \tau_{i-1}), \text{ where } b_1 = b \end{aligned} \qquad (7)$$

$$k_i = k' \times \mathrm{APD}_i \qquad (8)$$

The coefficient b_i indicates the final extraction yield obtained at previous i-1th heating step whereas the coefficient k_i is calculated based on the APD value at the ith heating step.

2.7. Evaluation of the applicability of the model

The extraction profile of constant-power MAE in Table 2 (No. 1) was used to calibrate the model's coefficients, i.e. the initial washing coefficient, b and the energy-based diffusion coefficient, k'. The coefficients were determined by curve-fitting Eq. (4) with the experimental data using Matlab curve fitting toolbox (version 2.1). The coefficients were then substituted into Eqs. 6–8 to predict the extraction curves of two-steps-power, intermittent-power and constant-temperature MAE as tabulated in Table 2 (Nos. 2–7) based on their APD values involved in the extraction. The goodness of fit for the predictions were evaluated based on the average relative error (%) by comparing with the experimental data. The total equilibrium extraction yields were determined by conducting the extraction using fresh sample in triplicate based on the heating conditions tabulated in Table 2.

3. Results and discussion

3.1. Calibration of model parameters

The initial washing coefficient b and the energy-based diffusion coefficient k' in Eq. (4) were calibrated based on constant-power MAE at 150 W as shown in Fig. 3. Approximately 56% out of total yield was obtained at the beginning of the extraction before heating. The coefficient k' (0.01279 mL/J) obtained at 150 W in this study is close to that reported at 100 W in the previous work (0.01452 mL/J) [13]. This suggests that the initial washing coefficient b and the energy-based diffusion coefficient k' are constant regardless of the heating power. Theoretically, they are affected only by the operating parameters such as extraction solvent, solvent to feed ratio and particle size of sample that have no direct effect on the microwave heating. This is because extraction solvent that affects the microwave absorption capability also at the same time, affects the solubility of the active compounds whereas solvent to feed ratio controls the accessibility of solvent to dissolve the compounds and sample particle size has an effect on the diffusion of the active compounds from the plant matrices. After calibration, the model coefficients obtained at $b = 0.5595$ and $k' = 0.01279$ mL/J were substituted in Eqs. 6–8 to predict the extraction profile of MAE conducted using various heating modes, heating powers and microwave systems.

3.2. Predictive capability of the generalized model

Based on constructed model Eqs. 6–8, the individual washing and diffusion coefficients of MAE at two steps power, intermittent power and constant temperature heating were calculated and tabulated in Table 3. All the predicted extraction profiles are able to capture the trends of the experimental extraction profiles as the average relative error in most cases was less than 4%. This indicates that the generalized model is feasible in predicting the MAE kinetics by adapting suitable diffusion coefficient according to the heating power involved in the extraction. As observed in Table 3, the diffusion coefficient k is strongly influenced by the heating power employed or the APD parameter. The performance of the generalized model, related extraction mechanism and the intrinsic effects of APD and AED parameters on each operational heating modes are elaborated accordingly.

3.2.1. Two-steps-power MAE

The extraction profiles of two-steps-power MAE at power configuration of 100–300 W and 300–100 W were predicted by the generalized model as depicted in Fig. 4. The extraction profiles exhibit similar trend with respect to their temperature profiles consisting of two distinct regions with different growth rates. Both the temperature and extraction profiles are dependent on the heat-

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