Modeling and prediction of extraction profile for microwave-assisted extraction based on absorbed microwave energy

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ABSTRACT:
A modeling technique based on absorbed microwave energy was proposed to model microwave-assisted extraction (MAE) of antioxidant compounds from cocoa (Theobroma cacao L.) leaves. By adapting suitable extraction model at the basis of microwave energy absorbed during extraction, the model can be developed to predict extraction profile of MAE at various microwave irradiation power (100-600 W) and solvent loading (100-300 ml). Verification with experimental data confirmed that the prediction was accurate in capturing the extraction profile of MAE (R-square value greater than 0.87). Besides, the predicted yields from the model showed good agreement with the experimental results with less than 10% deviation observed. Furthermore, suitable extraction times to ensure high extraction yield at various MAE conditions can be estimated based on absorbed microwave energy. The estimation is feasible as more than 85% of active compounds can be extracted when compared with the conventional extraction technique.

Keywords: absorbed power density, absorbed energy density, extraction model, extraction curve
1. Introduction
Microwave-assisted extraction (MAE) has been widely employed in the extraction of active compounds from plants due to its superior performance in terms of its extraction yields, solvent consumptions and extraction time (Chan, Yusoff, Ngoh, & Kung, 2011; Wang and Weller, 2006). Hence, MAE has the potential to replace conventional extraction techniques. Various extraction models for MAE have been developed to study the effects of operating parameters on the extraction kinetics. For instance, derivation from Fick’s law (Gujar, Wagh, & Gaikar, 2010), chemical kinetic equations (Xiao, Song, Wang, & Li, 2012; Spigno and De Faveri, 2009) and other empirical models (Amarni and Kadi, 2010) were employed and their extraction constants were reported for extraction of various active compounds from plants. However, the predictive capacity of such models is restricted to the extraction constants obtained using specific instrumental setup. Indirectly, this implies that the employment of such model to predict MAE profile (extraction yield vs. extraction time) of different instrumental setup would result in lack of fit. Moreover, the extraction constants were limited to certain operating conditions as the acquisition of experimental data for determining the constants of extraction models is time-consuming. Currently, the application of these kinetic models in the MAE is limited as the reported extraction constants, e.g. diffusivity, can only be used to indicate the kinetic of the extraction for comparison purpose such as at different operating conditions and extraction techniques (Gujar et al., 2010; Amarni and Kadi, 2010). To alleviate the shortcomings of the existing models, a new approach based on microwave energy absorbed in the extraction system is proposed in this work to model and predict the extraction profiles of MAE at various extraction conditions.

The microwave irradiation power for a given unit of extraction volume, known as “energy density”, is claimed to be more applicable for MAE study as compared to microwave power level (Alfaro, Belanger, Padilla, & Pare, 2003). It has been proven to be the most significant parameter in optimization studies (Li et al., 2012). However, the amount of power supply for the microwave heating does not reflect the actual power absorbed in the extraction system. Only some of the power will be absorbed and this depends on dielectric constant of the system (Mandal, Mohan, & Hemalatha, 2007). The energy absorbed in the extraction system is important as it provides localized heating to disrupt the cells and elute the active compounds (Sparr Eskilsson and Björklund, 2000). In this study, the microwave energy absorbed during extraction has been used to model MAE process and the crucial parameters such as solvent to feed ratio, applied microwave power and solvent loading have been included.
The model was employed to study MAE of antioxidant compounds from cocoa leaves. The theory on the development of the extraction model was presented and the developed model was employed to predict extraction curves of MAE at various extraction conditions. Predictive capability of the model was evaluated with experimental data. Furthermore, a technique for estimating suitable extraction time of MAE at equilibrium extraction was established. The feasibility of the estimation was evaluated by comparing its yield with the conventional extraction.

2. Material and method

2.1. Materials and reagents
Standards of antioxidant compounds, i.e. isoquercitrin (IQ), (-)-epicatechin (EC) and rutin (RT) were purchased from Sigma-Aldrich Co. (Malaysia). Acetonitrile and ethanol for chromatography analysis (HPLC grade) were purchased from Merck co. (Malaysia). The extraction solvent, denatured alcohol (EtOH) was purchased from LGC Scientific co. (Malaysia).

2.2. Extraction procedures
Fresh cocoa leaves were collected during pruning from local cocoa plantation in Pahang, Malaysia. The leaves were washed and dried in air drying oven at 40 °C for 24 hours until the moisture content of the dried leaves was 5-6%. The dried leaves were powdered and sieved to particle size of 0.25-0.60 mm. The plant sample was then stored in a storage container at 4 °C until further used in the extraction.

MAE was carried out in a domestic microwave oven with adjustable nominal power output (100-800 W) as the applied microwave power. The microwave oven was equipped with fiber optic Luxtron I652 thermometer to record the real time temperature profile during extraction. Cocoa leaves powder (1-6 g) was mixed with 85% aqueous EtOH (100-300 ml) to make up a desirable predetermined solvent to feed ratio in a 500 ml closed Duran bottle and was irradiated in the microwave oven at predetermined time duration without stirring. After extraction, the mixture was allowed to cool to room temperature by using water bath. The mixture was then subjected to filtration for removal of the plant residue. The extract obtained was filtered through
a 0.2 µm RC (Regenerated Cellulose) syringe filter for HPLC analysis. Extraction curve of MAE was constructed through series of extractions at the same operating conditions but with different extraction time using fresh sample. New batch of sample was taken from the storage container for the construction of each extraction curve. The effect of different batches of sample on the extraction curve of MAE was not studied in this work.

For comparison purpose, conventional Soxhlet extraction was also performed. Two grams (2 g) of dried sample powder was extracted with 200 ml solvent for 12 hrs in a Soxhlet apparatus for exhaustive extraction. The solvent used were pure EtOH and 85% EtOH aqueous solution. The subsequent analysis procedure was similar to the MAE as previously described. The experiment was conducted twice.

2.3. HPLC analysis
The quantifications of antioxidant compounds in the extracts were performed using an Agilent 1200 Series HPLC device with Agilent ZORBAX Eclipse Plus C18 column, 5 µm (4.6 mm × 150 mm). The HPLC method proposed by Bonaccorsi, Caristi, Gargiulli, and Leuzzi (2008) was used in this work. The mobile phase was 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 sample injection volume was 10 µL. The separation was conducted at 350 nm (IQ and EC) and 280 nm (RT) and was analysed using UV-DAD detector. The extraction yield was expressed as mass of extracted active compounds (mg) per mass of sample used (g). The total extraction yields of these antioxidant compounds (IQ, EC and RT) extracted from cocoa leaves (mg/g) were used as a response (Y and Y_sat) in this modeling study.

2.4. Determination of absorbed energy density (AED)
Hypothetically, MAE utilizes the absorbed microwave energy to achieve certain degree of extraction. As more microwave energy being absorbed by the extraction system, more active compounds are extracted until it reaches the equilibrium stage when there is no significant increase in extraction yields. In this study, total amount of microwave energy absorbed in the extraction solvent forms the basis for modeling of MAE process. Taking into account the effect of solvent loading on the absorption of microwave energy, absorbed energy density (AED) is being introduced as the total amount of microwave energy absorbed per unit volume of solvent used during MAE. The modeling of MAE process based on AED was demonstrated in this
A simple procedure to calculate AED by using absorbed power density (APD) is presented. APD is defined as microwave power absorbed per unit volume of solvent (W/ml). Unlike nominal microwave power which indicates the power setting of microwave setup, APD represents the actual microwave power being absorbed in the extraction solvent. In this study, APD of blank extraction solvent under different heating conditions, i.e. solvent loading (100-300 ml) and applied microwave power (100-600 W) were investigated. APD (W/ml) can be calculated as follows:

$$\text{APD} = \frac{Q}{V \cdot t_H}$$

where $Q$ is the total heat absorbed in the solvent during the microwave heating (J), $V$ is the solvent loading (ml) and $t_H$ is the microwave heating time (min). The total heat absorbed, $Q$ can be calculated from the temperature profiles of the solvent during microwave heating by using calorimetric method (Incropera, 2007) as shown in the following heating cases:

**Case A:** Final heating temperature $<$ boiling point of solvent

$$Q = m_L C_p \Delta T$$  

Eq. (2)

**Case B:** Final heating temperature = boiling point of solvent

$$Q = m_L C_p \Delta T + m_v H_{vap}$$

Eq. (3)

$m_L$ is the initial mass of the extraction solvent, $C_p$ is the heat capacity of the extraction solvent, $\Delta T$ is the differential temperature after microwave treatment, $m_v$ is the mass of the vaporized solvent, $H_{vap}$ is the heat of vaporization of the extraction solvent. Eq. (2) can be used to calculate the absorbed energy to increase the temperature of the extraction solvent from room temperature to boiling point ($\approx 70 ^\circ C$) while Eq. (3) includes both the energy required to heat and to vaporize the extraction solvent during boiling. To get representative APD values, microwave heating of blank extraction solvent were conducted at different heating times ($t_H$) to include both the heating cases. Then, the average values of APD at these conditions are determined. Example of calculated APD and $Q$ values are shown in Table 1:
### Table 1: APD values at different microwave irradiation power and solvent loading

<table>
<thead>
<tr>
<th>Solvent loading, V (ml)</th>
<th>Microwave irradiation power, P (W)</th>
<th>Absorbed power density, APD (W/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.43 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.93 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>2.24 ± 0.03</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.69 ± 0.10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.25 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.56 ± 0.06</td>
</tr>
<tr>
<td>250</td>
<td>100</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.37 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.48 ± 0.08</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.19 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.42 ± 0.08</td>
</tr>
</tbody>
</table>

Example of calculation of APD by calorimetric method

<table>
<thead>
<tr>
<th>MAE operating conditions</th>
<th>Heating time, $t_H$ (min)</th>
<th>Total heat absorbed, Q (J)</th>
<th>Absorbed power density, APD (W/ml)</th>
<th>Average APD (W/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ml, 100 W</td>
<td>5.00</td>
<td>5266</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>13.00</td>
<td>10796</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.00</td>
<td>23649</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

The average values of APD at solvent loading (100-300 ml) and applied microwave power (100-600 W) are tabulated in Table 1. Depending on the extraction conditions, AED values of extraction solvent during MAE process can be determined as follows:

\[
AED_t = APD \times t
\]

where $AED_t$ is the total amount of microwave energy absorbed per volume of solvent loading during the extraction (J/ml) and $t$ is the extraction time (min). The modeling of extraction profile of MAE based on AED will be described in the following section.

### 2.5. The development of model

The extraction profile of MAE plotted with respect to AED would exhibit similar trends as those observed in typical dynamic extraction profiles (yield vs time), where two distinct phases are observed, i.e. washing and diffusion steps, respectively. Since the prediction of the washing step is known to be challenging (as the period of constant extraction rate is hardly determined...
(Franco, Sineiro, Pinelo, & Núñez, 2007), only the diffusion step will be investigated in this work. This is also motivated by the fact that the determination of equilibrium extraction yields is relatively more important than the yields associated with washing step. The film theory (Velickovic, Milenovic, Ristic, & Veljkovic, 2008; Stanisavljević, Lazić, & Veljković, 2007) is usually employed for the modeling of typical extraction curve (yields vs. extraction time) as follows:

**Original film theory**

\[
\frac{Y}{Y_s} = 1 - (1 - b) \exp(-k \cdot t)
\]

**Eq. (5)**

where \( Y \) is the extraction yield (mg/g), \( Y_s \) is the equilibrium extraction yield (mg/g), \( b \) characterizes the washing step while \( k \) characterizes the diffusion step (min\(^{-1}\)). In this work, film theory in Eq. (5) was adapted using the basis of AED\(_t\). Unlike extraction time, AED\(_t\) not only indicates the progress of an extraction but it also gives additional information on the microwave power absorbed in the extraction system. The adapted model is shown in Eq. (6).

**Adaptation of film theory**

\[
\frac{Y}{Y_s} = 1 - (1 - b') \exp(-k' \cdot AED\(_t\))
\]

**Eq. (6)**

where \( b' \) characterizes the washing step while \( k' \) characterizes the diffusion step both in absorbed energy basis ((J/ml)\(^{-1}\)). The washing and diffusion constants (\( b' \) and \( k' \)) are independent on the operating parameters that have influences on the absorption of microwave energy such as solvent loading, applied microwave power and etc., as the effects of these operating parameters are exerted on the AED\(_t\) value (due to APD value). However, the constants are affected by other operating parameters such as solvent to feed ratio, particle sizes and etc., which are not related to the absorption of microwave energy. Eq. (6) was employed to determine the constant \( b' \) and \( k' \) by fitting with experimental extraction curve. The experimental data was converted to absorbed energy basis prior to the curve fitting.

Once the constant \( b' \) and \( k' \) are obtained for a particular operating condition, Eq. (6) can be further developed to predict the dynamic extraction profile (yields vs. extraction time) under various applied microwave power and solvent loading. This was done by substituting Eq. (4) in Eq. (6) to convert the adapted model to extraction time basis as shown in Eq.(7)

\[
\frac{Y}{Y_s} = 1 - (1 - b') \exp(-k' \cdot APD \cdot t)
\]

**Eq. (7)**
Eq. (7) can be used to predict the extraction profiles of MAE (at extraction time basis) at various operating conditions by substituting the APD value at the respective conditions. APD indicates the interaction effect of microwave irradiation power and solvent loading during MAE. By comparing the coefficients of the proposed model in Eq. (7) with the original film theory in Eq. (5), the washing coefficient for both the models is the same, $b = b'$, while the diffusion coefficient of the original film theory equation, $k$ is equivalent to $k' \times APD$.

2.6. The modeling procedure and design of experiments

As mentioned previously, film theory was adapted to model MAE with AED as a basis. The effects of solvent to feed ratio (20-80 ml/g) on the constant $b'$ and $k'$ in the adapted model in Eq. (6) were investigated. The constants were determined by fitting Eq. (6) with the experimental extraction profile in Table 2 (no. 1-3) at AED basis by using Matlab curve fitting toolbox (version 2.1). The constants were then substituted into Eq. (7) to predict extraction curves of MAE at various extraction conditions. In this study, the prediction of extraction curve by the proposed model was performed under various applied microwave power (100-600 W) and solvent loading (100-300 ml) as shown in Table 2 (no. 4-9). The goodness of fit for the predicted extraction curve was evaluated by comparing with the experimental extraction curves. The model was then used to predict the constants of film theory ($b$ and $k$). The predicted constants were compared with that obtained by fitting the actual film theory of Eq. (5) with the experimental extraction curve. In addition, suitable extraction times of MAE at various extraction conditions were estimated from the modeling result. The extraction time was estimated such that the extraction was in the equilibrium stage. The corresponding extraction yields were then compared with conventional Soxhlet extraction to evaluate the feasibility of the estimation.
Table 2: Experimental design for extraction curves of MAE

<table>
<thead>
<tr>
<th>Extraction conditions</th>
<th>Equilibrium extraction yields (mg/g)</th>
<th>Total equilibrium extraction yields, $Y_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IQ</td>
<td>EC</td>
</tr>
<tr>
<td>1 5 g sample, 100 ml, 100 W, 30 min $^a$</td>
<td>2.63 ± 0.03</td>
<td>2.15 ± 0.03</td>
</tr>
<tr>
<td>2 2 g sample, 100 ml, 100 W, 35 min $^a$</td>
<td>2.89 ± 0.01</td>
<td>2.58 ± 0.05</td>
</tr>
<tr>
<td>3 1.25 g sample, 100 ml, 100 W, 30 min $^a$</td>
<td>3.09 ± 0.11</td>
<td>2.52 ± 0.01</td>
</tr>
<tr>
<td>4 2 g sample, 100 ml, 200 W, 19 min $^a$</td>
<td>3.06 ± 0.06</td>
<td>2.57 ± 0.06</td>
</tr>
<tr>
<td>5 2 g sample, 100 ml, 300 W, 9 min $^a$</td>
<td>2.85 ± 0.04</td>
<td>2.45 ± 0.08</td>
</tr>
<tr>
<td>6 2 g sample, 100 ml, 600 W, 4 min $^a$</td>
<td>2.75 ± 0.04</td>
<td>2.36 ± 0.04</td>
</tr>
<tr>
<td>7 4 g sample, 200 ml, 200 W, 35 min $^a$</td>
<td>3.19 ± 0.01</td>
<td>2.79 ± 0.08</td>
</tr>
<tr>
<td>8 5 g sample, 250 ml, 250 W, 8 min $^a$</td>
<td>3.19 ± 0.04</td>
<td>2.57 ± 0.03</td>
</tr>
<tr>
<td>9 6 g sample, 300 ml, 300 W, 10 min $^a$</td>
<td>2.92 ± 0.06</td>
<td>2.61 ± 0.03</td>
</tr>
</tbody>
</table>

$^a$ total extraction time.

3. Results and discussion

3.1. AED extraction model

The extraction constants ($b'$ and $k'$) in Eq. (6) under influence of AED are strongly influenced by other parameters such as sample preparation techniques, e.g. sample drying and grinding (So and Macdonald, 1986), solvent concentration and solvent to feed ratio. In this study, the effect of solvent to feed ratio (20-80 ml/g) on the extraction constants was investigated. The extraction constants at these solvent to feed ratios were determined by fitting Eq. (6) with the extraction profile as illustrated in Fig. 1. The extraction constants, $b'$ and $k'$ obtained from the non-linear regression indicate that all the extraction curves (20-80 ml/g) fitted well with the adapted model (Eq. (6)) as shown in Fig. 1.

From the extraction profile of MAE at different solvent to feed ratio as shown in Fig. 1, MAE at different solvent to feed ratio gives different extraction profile and the equilibrium extraction yield increased with solvent to feed ratio. At low solvent to feed ratio, the mass transfer barrier affects the diffusion of active compounds from the plant cell which resulted in poor extraction yield (Qu, Pan, & Ma, 2010; Franco, Pinelo, Sineiro, & Núñez, 2007). In other words, high solvent to feed ratio would enhance the diffusion step ($k'$). In view of the kinetic of the extraction, the equilibrium extraction yield of 20 ml/g solvent to feed ratio was lower than that
in 50 ml/g despite that the diffusion constant \((k')\) of the former extraction was higher. This is probably caused by the saturation of extraction solvent at 20 ml/g which has shortened the time for the extractions to reach the equilibrium stage (resulted in higher \(k'\) value). Considering both the economical and feasibility aspects, solvent to feed ratio of 50 ml/g was selected and the predictive capability of the proposed model at this solvent to feed ratio was evaluated in subsequent modeling study.

![Fig. 1: Curve fitting of extraction profiles of MAE with the proposed model in Eq. (6) for solvent to feed ratio (● 20 ml/g, ○ 50 ml/g and ▼ 80 ml/g) under applied microwave power of 100 W and solvent loading of 100 ml (APD of 0.15 W/ml). The constant \(b'\) and \(k'\) were determined with 95\% confidence bounds.](image)

3.2. Predictive capability of AED extraction model

The extraction model in Eq. (7) was constructed by using the constant \(b'\) and \(k'\) at solvent to feed ratio of 50 ml/g. The model is expressed in extraction time (min) and APD (W/ml) as shown:

\[
\frac{Y}{Y_s} = 1 - (1 - 0.5436) \exp(-0.8712 \times APD \times t)
\]

Eq. (8)

Based on APD, Eq. (8) was employed to predict the extraction profile of MAE under various solvent loading and applied microwave power as illustrated in Fig. 2. This figure shows that all the predicted extraction curves are capable of capturing the trend of the experimental
extraction profiles. This signifies that the diffusion step of MAE can be characterized by APD of the extraction system. In addition, Fig. 2 shows that the washing step of MAE is capable of extracting 53% out of the total extraction yield regardless of the operating condition employed. This suggests that the constant $b'$, which characterizes the washing step of extraction, remain unchanged irrespective of various solvent loading and applied microwave power.

The modeling approach can also be used to predict the coefficients of the extraction model of interest. As the film theory was adapted, the coefficients of the original model ($b$ and $k$) can be determined by comparing it with the adapted model (Eq. (5) vs. Eq. (8)). The diffusion constant in film theory, $k$ is analogous to $k' \times APD$ in Eq. (5) while the coefficient of washing step remain unchanged, $b = b' = 0.5436$. The extraction constants ($b$ and $k$) of film theory predicted by using this modeling approach are shown in Fig. 2. The comparison of the predicted constants and the constants obtained by fitting with original film theory shows that the proposed method is feasible as the deviations between the two constants was less than 10% in most of the cases. The only one prediction shows deviations around 40% could have due to the variation of the amount of active compounds in the plant sample. Nevertheless, the extraction profile of MAE still can be predicted in this case with r-square value of 0.88 (Fig. 2(a)). This further confirms that by the modeling method reliable in predicting extraction curve of MAE. The APD values used for the prediction are obtained based on the microwave power absorbed in the extraction solvent without considering the effect of microwave heating on the plant material and the interactive effect between the plant material and extraction solvent. When extraction involves sample with high moisture content, the determination of APD value should take into the account of both the microwave heating on the extraction solvent and plant material as the sample can possibly absorb significant microwave energy.

It is apparent that $k$ increases with APD of extraction system (since $k$ is analogous to $k' \times APD$). This suggested that high APD value can enhance diffusion thus shorten the extraction time. For instance, the total extraction time required to reach equilibrium extraction yield was reduced by 10 folds from 20 min to 2 min when the APD values increased from 0.25 W/ml to 2.24 W/ml (refer Fig. 2). However, about 10% loss of equilibrium extraction yield was observed when APD was increased to 2.24 W/ml (refer to Table 2). This implied that thermal degradation of active compounds might have occurred at high APD.
Fig. 2: Prediction of extraction curves by using Eq. (7) for the following extraction conditions: a) 2 g sample, 100 ml, 200 W (APD of 0.43W/ml); b) 2 g sample, 100 ml, 300 W (APD of 0.93W/ml); c) 2 g sample, 100 ml, 600 W (APD of 2.24 W/ml); d) 4 g sample, 200 ml, 200 W (APD of 0.25W/ml); e) 5 g sample, 250 ml, 250 W (APD of 0.37W/ml); f) 6 g sample, 300 ml, 300 W (APD of 0.42W/ml). The equations displayed are in term of extraction time, $t$ (min).
So far, the results showed that the model is capable of modeling the extraction profile of MAE in term of degree of extraction ($Y/Y_{\text{sat}}$). Since there is only a slight 10% decrease of total extraction yield under influence of APD, the model in Eq. (8) can be used to predict extraction yield (mg/g) of MAE under various extraction conditions based on equilibrium extraction yield, $Y_{\text{sat}}$. The equilibrium yield of 11.24 mg/g in Table 2 (no. 2) was used for the prediction as the proposed model was developed from this extraction curve. The predictions of extraction yield of MAE for various extraction conditions under 50 ml/g are shown in Table 3. All the predicted yields were close to the experimental values with deviations generally less than 10% demonstrated the model is reliable.

Table 3: Experimental and predicted extraction yields of MAE and their comparison with Soxhlet extraction

<table>
<thead>
<tr>
<th>MAE conditions</th>
<th>APD (W/ml)</th>
<th>AED (J/ml)</th>
<th>Predicted degree of extraction, $Y/Y_{\text{sat}}$</th>
<th>Predicted extraction yield (mg/g)</th>
<th>Experimental extraction yields (mg/g)</th>
<th>Percentage deviation of the predicted yield (%)</th>
<th>Recovery (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 g sample, 150 ml, 100 W, 18 min</td>
<td>0.12</td>
<td>130</td>
<td>0.93</td>
<td>10.46</td>
<td>11.28 ± 0.48</td>
<td>7.4</td>
<td>97</td>
</tr>
<tr>
<td>3 g sample, 150 ml, 300 W, 6 min</td>
<td>0.69</td>
<td>248</td>
<td>0.99</td>
<td>11.10</td>
<td>10.03 ± 0.35</td>
<td>11.0</td>
<td>86</td>
</tr>
<tr>
<td>4 g sample, 200 ml, 100 W, 20 min</td>
<td>0.1</td>
<td>120</td>
<td>0.92</td>
<td>10.34</td>
<td>11.49 ± 0.16</td>
<td>10.1</td>
<td>99</td>
</tr>
<tr>
<td>4 g sample, 200 ml, 300 W, 7.2 min</td>
<td>0.56</td>
<td>242</td>
<td>0.99</td>
<td>11.09</td>
<td>10.96 ± 0.21</td>
<td>0.8</td>
<td>94</td>
</tr>
<tr>
<td>5 g sample, 250 ml, 100 W, 17.5 min</td>
<td>0.08</td>
<td>84</td>
<td>0.87</td>
<td>9.73</td>
<td>10.76 ± 0.80</td>
<td>10.0</td>
<td>93</td>
</tr>
<tr>
<td>5 g sample, 250 ml, 300 W, 6.5 min</td>
<td>0.48</td>
<td>187</td>
<td>0.97</td>
<td>10.90</td>
<td>10.12 ± 0.41</td>
<td>7.9</td>
<td>86</td>
</tr>
<tr>
<td>6 g sample, 300 ml, 100 W, 18 min</td>
<td>0.07</td>
<td>76</td>
<td>0.85</td>
<td>9.53</td>
<td>10.55 ± 0.63</td>
<td>10.1</td>
<td>91</td>
</tr>
<tr>
<td>6 g sample, 300 ml, 200 W, 12 min</td>
<td>0.19</td>
<td>137</td>
<td>0.94</td>
<td>10.54</td>
<td>10.66 ± 0.17</td>
<td>0.6</td>
<td>91</td>
</tr>
<tr>
<td>Soxhlet conditions</td>
<td>Total extraction yields (mg/g)</td>
<td></td>
<td></td>
<td></td>
<td>9.95 ± 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 g sample, ETOH, 200 ml, 12 hr</td>
<td>2 g sample, ETOH, 200 ml, 12 hr</td>
<td></td>
<td></td>
<td></td>
<td>11.67 ± 0.41</td>
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</tr>
</tbody>
</table>

\[ a \] Predicted extraction yield was calculated based on equilibrium extraction yield of MAE at 2 g, 100 ml, 100 W (11.24 mg/g). \[ b \] The recovery of total extraction yield (%) was calculated based on Soxhlet extraction (total extraction yields of 11.67 mg/g).

3.3. **Estimation of suitable extraction time of MAE based on AED**

To further investigate the effect of microwave energy absorbed in the MAE system on the extraction kinetics, the experimental yields at various operating conditions were plotted with respect to the amount of absorbed energy as shown in Fig. 3. As illustrated in this figure, all the scattered experimental points exhibit the same extraction trend. This suggested that the extraction stage of MAE is strongly dependent on AED. In this study, three extraction regions in the diffusion step were identified as shown in Fig. 3. The first region describes a constant rate of diffusive extraction where the diffusion of active compounds to the extraction solvent
takes place steadily. The microwave energy associated to this region was below 100 J/ml. The diffusion rate decreased as the extraction prolongs to reach equilibrium. Further increment in the microwave energy beyond 300 J/ml vaporize more than 20% (vol) of extraction solvent without give any noticeable increase in extraction yields. Conversely, a slight decrement in the extraction yields was observed and it might be caused by thermal degradation when the extraction system was subjected to excessive microwave heating (Fig. 3). Thus, it is suggested that the range of energy required to reach equilibrium stage ($AED_{eq}$) for MAE of antioxidant compounds from cocoa leaves was 100-300 J/ml.

Suitable extraction time of MAE can be estimated from $AED_{eq}$ on the ground that $AED_{eq}$ denotes the microwave energy required to reach equilibrium stage regardless of the solvent volume and it also indicates the progress of extraction with time. The estimated extraction time can be calculated using expression as follows:

$$t_e = \frac{AED_{eq}}{APD}$$

Eq. (9)

where $t_e$ denotes the estimated extraction time. Suitable extraction time of MAE can be
estimated by knowing the APD values of the designated operating conditions. For evaluation purpose, MAE at solvent to feed ratio of 50 ml/g under various solvent loading and applied microwave power were conducted along the region of AED$_{eq}$ as shown in Table 3. The corresponding extraction yields were compared with that obtained from exhaustive Soxhlet extraction. The comparative study shows that the total antioxidant compounds in the range of 85-99% can be recovered when MAE was conducted in the equilibrium extraction region. This suggests that the estimation method is feasible and can be employed to determine the optimum extraction time of MAE.

4. Conclusion
A modeling technique based on absorbed microwave energy is proposed. The developed AED-model exhibits high predictive capability in capturing the trend of the extraction profile of MAE. The development of extraction model based on the technique mentioned involves less experimental data as the coefficients of the model can be determined from the APD of the extraction system according to the extraction conditions. In other words, the APD values can be used to characterize the MAE profile. Similar MAE profile can be possibly obtained for different microwave setup by adjusting the applied microwave power to the designated APD value. As a conclusion, this AED-based extraction model is reliable and could be applied to various microwave extractors and it is useful for scaling up process. In addition, estimation of suitable extraction time of MAE based on AED for equilibrium extraction is feasible and which can be used to determine the range of extraction conditions prior to the optimization study.

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