Mathematical modeling of mass transfer in supercritical fluid extraction of patchouli oil

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Funding information
Ministry of Education - Singapore, Grant/Award Number: MOE2015-TIF-2-G-051

Patchouli oil is a high-value essential oil used in cosmetic, food, and pharmaceutical industries. In this work, supercritical fluid extraction of patchouli oil with various operating process parameters (pressure, temperature, flow rate, and particle size) were studied and the results were modeled using the broken and intact cell model (BICM). From the experimental studies, it was found that the extraction rate was improved at higher pressures and flow rates, where the mass transfer resistances in the liquid and solid phase were decreased; however, the increase in temperature had an inverse effect on extraction rate and mass transfer. In the case of particle size, a moderate size of 0.3 to 0.6 mm gave the optimal extraction rate. The BICM predictions showed good agreements with experimental data and gave valuable insights regarding the mass transfer mechanism of the extraction process, including mass transfer coefficients and extraction periods governed by convection and diffusion.

KEYWORDS
mass transfer, mathematical modeling, patchouli, supercritical fluid extraction

1 INTRODUCTION

Patchouli (Pogostemon cablin) is an aromatic species of the Lamiaceae, native to South East Asia, that contains essential oil that is of great economic value.1 Patchouli oil is ranked in the top 18 out of 300 essential oils of commercial importance in the world.2 Due to the dominant aromatic spicy fragrance, patchouli oil is highly appreciated in perfumery and aromatherapy.3 Furthermore, it is known to possess numerous potential therapeutic properties such as antimicrobial, anti-inflammatory, and antioxidant activities.4-6 Patchouli oil is traditionally obtained from steam distillation of dried patchouli leaves, which involves high temperature and long extraction time to recover a satisfactory amount of oil. A typical steam distillation process in Indonesia requires 40 L of kerosene for an 8 hour extraction, which recovers 2.2 to 2.8 kg of oil per 100 kg leaves.7 Therefore, an alternative extraction method with the minimum use of energy, solvent, and time is of considerable interest.

Few studies described the supercritical fluid extraction (SFE) of patchouli oil with CO2 as a promising technology for production of patchouli oil.8-10 Experimental studies from the SFE and steam distillation on patchouli leaves showed promising results for SFE in terms of yield and quality.10 Patchouli oil can be extracted from the stems, leaves, and flowers of patchouli plant,9 though the patchouli oil content was found to be higher from patchouli leaves than from the stems.8 Experimental optimization studies for extraction of patchouli oil based on yield were 18 MPa at 312 K as determined by
Liu et al.\textsuperscript{8} and 20 MPa at 318 K as determined by Xiong et al.\textsuperscript{9} The SFE process can be influenced by several variables for extraction and composition of the extract. In optimization of the SFE process, it is important to understand the effect of process variable on extraction yield and the quality of the extract.\textsuperscript{11}

SFE is a green extraction method that uses CO\textsubscript{2} above its critical temperature of 304 K and critical pressure of 7.39 MPa to produce solvent-free extracts at low temperatures.\textsuperscript{12-14} The nonpolarity of supercritical CO\textsubscript{2} makes it suitable and promising for the extraction of lipophilic substances such as essential oils. However, this technology is rarely used industrially for the extraction of essential oils mainly due to the high investment required for SFE plants\textsuperscript{15} in contrast to the simple design of conventional steam distillation processes. In recent years, there has been research focused on the comparison of the yield and quality of extraction from conventional steam and hydrodistillation processes with SFE.\textsuperscript{10,16} These studies aim to provide information and evidence for the use of SFE as a greener and more efficient alternative.

Hence, tools that are helpful to process design decision makers are necessary, such as the modeling of the extraction phenomena occurring inside the extraction vessel.\textsuperscript{17} Numerous efforts have been made to mathematically simulate SFE processes in terms of the time dependent extraction curves (overall extraction curves [OEC]).\textsuperscript{17-21} For the proper design of SFE processes, it is important to have a comprehensive knowledge of the mass transfer mechanism of the extraction process with the suitable mathematical representation.\textsuperscript{22} Furthermore, it is important to study the kinetic model that gives large-scale OEC with minimum error using the fitting parameters obtained from modeling of small scale experiments.\textsuperscript{18,23}

In this study, the broken and intact cell model (BICM) by Sovová\textsuperscript{24-26} was considered for a comprehensive phenomenological model. This model enables to investigate valuable information regarding the dominant transport mechanisms, the characteristic extraction periods of the process, and relevant parameters involving kinetics, equilibrium, and biomass features.\textsuperscript{22,24} The BICM was typically suitable for natural materials such as seeds, leaves, peels, etc, where the material had to be pretreated by milling to a desired size range before extraction. This was because the BICM described the situation where some of the extract was present on the outer surfaces of the particles or in cells that were broken, and part of the extract remains more deeply within pores or inside cells that were intact.\textsuperscript{22,26} Other models used to describe the extraction kinetics for SFE process include the hot sphere diffusion model, shrinking core model, as well as theoretical models such as the diffusion layer model, desorption model, and portioning coefficient model.\textsuperscript{22}

The aim of this paper was to study the SFE of patchouli oil using a preparative-scale setup with CO\textsubscript{2} recycler, evaluating important variables for scale-up development, including the particle size range, pressure, and temperature. The mathematical modeling was carried out to provide an understanding of the physical properties of the patchouli particles and patchouli oil investigated in this study. The kinetics and mass transport phenomena of the extraction process will be useful in the future evaluation of the process in scale-up design and development.

2 MATERIALS AND METHODS

2.1 Sample preparation

Dried patchouli leaves with a moisture content of 10.60 ± 0.07\%, were obtained from Indonesia. The leaves were milled using an electric grinder and sifted accordingly to three different groups of particle size range ($d_p$), which consists of (1) 0 to 0.15 mm, (2) 0.3 to 0.6 mm, and (3) 0.84 to 1.19 mm, using mechanical sieves of corresponding mesh size. Samples were packed and stored at room temperature until utilization. Liquid CO\textsubscript{2} with a purity of 99.5\% was obtained from Air Liquide Singapore Pte Ltd and n-hexane of analytical grade was obtained from Fischer Scientific Pte Ltd (Singapore).

2.2 Supercritical fluid extraction

The experiments were performed using a customized SFE system (Model SFE 1000 System, Waters Corporation, USA) with a CO\textsubscript{2} recycler. Figure 1 shows a schematic diagram of the SFE setup. A 0.001-m\textsuperscript{3} extraction vessel was loaded with 50-g ground material and glass beads to form a packed bed. The evaluated operational variables were pressure (9-15 MPa), temperature (308-318 K), solvent flow rate (0.0833-0.2500 g·s\textsuperscript{-1}), and particle size (0.15 mm, 0.3-0.6 mm, and 0.84-1.19 mm). CO\textsubscript{2} was pumped to the extraction vessel at various flow rates using a high-pressure liquid CO\textsubscript{2} pump. The pressures in the extraction and collection vessels were controlled using backpressure regulators. The pressure in the collection vessel was held at 6.6 MPa, below the critical pressure of CO\textsubscript{2}, for oil separation and recycling of CO\textsubscript{2}. Temperature in the extraction and collection vessels were kept constant (± 1 K) using band heaters. The temperature in the collection vessel was kept constant at 313 K. All SFE experiments were ran in dynamic mode for a duration of 240 minutes. CO\textsubscript{2} extracts were collected and weighed gravimetrically at 10-minute intervals. Extraction experiments were done in
duplicates and the average weight of oil at each time interval was summed up to determine the cumulative weight of all samples.

2.3 Broken and intact cell model

The BICM proposed by Sovová26 has been the most adopted approach in SFE comprehensive modeling. It is devoted to matrices submitted to milling in which two distinct domains are left to be extracted: cells with broken walls and intact cells.18,24,27 The total extractable solute in the matrix ($o$) is divided into two portions: easily accessible solute ($p$) and the hardly accessible solute ($k$). The easily accessible solute in the broken cells is removed by convection to the extraction fluid and the extraction kinetics is dependent on the solubility of the analytes in the solvent. In contrast, the removal of hardly accessible solute from the intact cells is driven by diffusion from inner intact cells to the outer broken cells.

In this model, the OEC of SFE processes are described in three periods controlled by different mass transfer mechanisms, namely, the constant extraction rate (CER) period, the falling extraction rate (FER) period, and the diffusion-controlled (DC) period. The CER is a fast extraction rate where the extraction mechanism is governed by convection as the external surface of the particles is covered with easily accessible solute. During the FER period, the extraction rate encounters a transition from the CER to the DC, where the easily accessible solute at external surface start to exhaust and mass transfer resistance in the solid-fluid interface begins. In the DC period, also known as slow-extraction period, the easily accessible solute at the external surface diminishes fully. Therefore, the extraction rate is governed exclusively by diffusion mechanism where less accessible solute at the core of the particles diffuses through pores and finally transports to the bulk fluid. The analytical solution of BICM is described by the following equations, where the OEC is a function of time.

$$m_t = Q_{CO_2}Y^* \left[ 1 - \exp \left( -Z \right) \right] t, \quad \text{if} \quad 0 \leq t \leq t_{CER}$$  \hspace{1cm} (1a)

$$m_t = Q_{CO_2}Y^* \left[ t - t_{CER} \exp \left( z_w - Z \right) \right], \quad \text{if} \quad t_{CER} \leq t \leq t_{FER}$$  \hspace{1cm} (1b)

$$m_t = N \left[ x_o - \frac{Y^*}{W} \ln \left\{ 1 + \left[ \frac{\exp \left( Wx_o \right)}{Y^*} - 1 \right] \exp \left[ \frac{WQ_{CO_2}N}{x_o} \left( t_{CER} - t \right) \frac{x_k}{x_o} \right] \right\} \right], \quad \text{if} \quad t > t_{FER}$$  \hspace{1cm} (1c)

$x_o$ is the sum of two fractions $x_p$ and $x_k$, which represent the fraction of easily accessible solute and hardly accessible solute present in the matrix over the nonextractable solute, respectively. $Q_{CO_2}$ is solvent mass flow rate (g s$^{-1}$), $N$ is mass of nonextractable solid (g), $Y^*$ is solubility (g oil g CO$_2$$^{-1}$), and $Z$ is a dimensionless variable. In the FER, the exhaustion of easily accessible oil in the raw material is given by a dimensionless variable $z_w$ and is defined in Equation (2).

$$z_w = \frac{ZY^*}{Wx_o} \ln \left[ \frac{x_o \exp \left( WQ_{CO_2} \left( t_{CER} - t \right) / N \right) - x_k}{x_o - x_k} \right] \quad (2)$$

$t_{CER}$ (s) signals the end of the CER and the beginning of the FER. $t_{FER}$ (s) represents the end of the transition period with $z_w = 0$ at the start and $z_w = Z$ at the $t_{FER}$. The values of $t_{CER}$ and $t_{FER}$ are determined by Equations (3) and (4), respectively.

$$t_{CER} = \frac{(x_o - x_k)N}{Y^*ZQ_{CO_2}}$$  \hspace{1cm} (3)
The parameters $Z$ and $W$ are directly proportional to fluid and solid phase mass transfer coefficient, respectively, and are given by Equations (5) and (6)

\[ Z = \frac{Nk_{Ya}\rho_{CO_2}}{Q_{CO_2}(1-\varepsilon)\rho_s} \]

\[ W = \frac{Nk_{Xa}Q_{CO_2}(1-\varepsilon)}{(1-\varepsilon)} \]

where $k_{Ya}$ and $k_{Xa}$ are mass transfer coefficients in the fluid and solid phase (s$^{-1}$), respectively, $\rho_s$ and $\rho_{CO_2}$ represent the density of the leaves and supercritical carbon dioxide (kg m$^{-3}$), respectively, and $\varepsilon$ represents bed void fraction.

The adjustable parameters $Z$, $W$, and $x_k$ were optimized to fit experimental data by minimizing absolute average relative deviation (AARD) as the objective function in the following Equation (7) using MATLAB.

\[
\text{AARD} \ (%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{m_i - m_{i,\text{exp}}}{m_{i,\text{exp}}} \right|
\]

3 | RESULTS AND DISCUSSION

3.1 | Obtaining parameters for modeling

The solubility ($Y^*$) of patchouli oil in the extraction fluid, directly proportional to the extraction rate, was obtained from the first and linear part of each corresponding OEC.\textsuperscript{18} A Soxhlet extraction with n-hexane has been performed on ground patchouli leaves to determine the hexane-extractable oil content and 11.76 ± 0.09$\%$ was obtained. Therefore, for 50 g of material, the mass of nonextractable solid ($N$) was 44.12 g and the amount of initial solute content per nonextractable solute ($x_o$) in the patchouli leaves was 0.1332 g oil per g of nonextractable material. For the particles of 0-0.15 mm, 0.3-0.6 mm, and 0.84-1.19 mm, the fixed beds had bulk densities ($\rho_b$) of 283.95, 199.1, and 176.05 kg m$^{-3}$, respectively, and the corresponding particle densities ($\rho_s$) are 479.17, 360.87, and 297.08 kg m$^{-3}$. The values of porosity were 0.407, 0.448, and 0.407, respectively, obtained by $(1 - (\rho_b/\rho_s))$.

3.2 | Effect of operating variables on mass transfer in SFE of patchouli oil

The pressure range of 9 to 15 MPa was chosen because higher pressures tend to reduce selectivity due to the extraction of undesirable components in terms of the oil quality, such as cuticular waxes.\textsuperscript{10} The temperature range of 309 to 318 K was selected to limit the degradation of thermally labile compounds.

3.2.1 | Effect of pressure

Figure 2 shows the effect of pressure from 9 to 15 MPa on the extraction of patchouli oil using temperature of 313 K, flow rate of 0.1667 g s$^{-1}$ and particle size between 0.3 and 0.6 mm. A faster extraction rate was observed when the pressure increased. A higher pressure enhanced the cumulative weight of oil due to the improved density and solvation strength of the supercritical fluid. The steeper initial slopes of the OEC at higher pressures indicate that solubility was improved. The total extraction yield obtained after 240 minutes is about 1.7 times as pressure increases from 9 to 15 MPa. The model curves fitted adequately to experimental data with fully consistent trend.

Table 1 shows the solubility ($Y^*$) model parameters ($Z$, $W$, $x_k$), time of CER ($t_{CER}$), time of FER ($t_{FER}$) mass transfer coefficients in the fluid phase ($k_{Ya}$) and the solid phase ($k_{Xa}$), and AARD obtained at different pressures. At 15 MPa, the oil extracted at the end of the transition period ($t = t_{FER} = 37.12$ minutes) was approximately 65$\%$ of total oil extracted. Up to the $t_{FER}$, the mass transfer was governed initially by convection before gradually transiting to intraparticle diffusion. The remaining 35$\%$ oil was extracted in the third period ($t \geq t_{FER}$) where mass transfer was controlled by solely diffusion. Therefore, it may be more cost efficient to end the extraction at the $t_{FER}$ as it only required 37 minutes to extract 65$\%$ of the total oil in contrast to the later 203 minutes for the extraction of the remaining 35$. For SFE at 9 and 12 MPa, about 85%
and 70% of extraction yield were obtained at $t = t_{FER}$ (133.7 minutes and 61.48 minutes), respectively. The internal and external mass transfer resistances were evaluated by the values of $k_{Xa}$ and $k_{Ya}$, respectively. Table 1 shows that $k_{Xa}$ is lower than $k_{Ya}$ for all experiments. The solute situated inside the particles take longer to cross the solid-fluid interface than the solute located on particle surface, reducing the mass transfer coefficient in solid phase $k_{Xa}$. Hence, low $k_{Xa}$ values suggest that the diffusional mechanism is less representative than the convection on SFE of patchouli oil. As pressure increased from 9 to 15 MPa, the solubility of patchouli oil in the extraction fluid increased. Therefore, the mass transfer coefficients in the fluid phase ($k_{Ya}$), which governs the convection phenomena increased. Furthermore, at higher pressures, there was a decrease in mass transfer resistance in the solid phase as mass transfer coefficients in the solid phase ($k_{Xa}$) increased.

### 3.2.2 Effect of temperature

The effect of temperature from 308 to 318 K on the SFE of patchouli oil was evaluated by using materials of particle size between 0.3 and 0.6 mm at pressure of 12 MPa and flow rate of 0.1667 g·s$^{-1}$ as shown in Figure 3. At constant pressure, an increase in temperature reduced the density of supercritical CO$_2$, therefore diminishing the solvent power of supercritical CO$_2$. However, an increase in temperature increased vapor pressure of the compounds and makes them easier to extract. These two competing effects are dependent on extraction conditions. Above the crossover pressure, the effect of temperature on solute vapor pressure predominates that of density. Therefore, the yield tends to increase with temperature. Below the crossover pressure, the effect of temperature on density is greater than that of solute vapor pressure. Previous studies have shown that crossover phenomenon was observed at high pressure ($\geq$20 MPa), while extraction temperature was increased.

In this study, since pressure was set at relatively low pressure (9-15 MPa), the crossover phenomenon was not observed. Hence, the effect on temperature on density outweighed that of solute vapor pressure. The total extraction yield obtained after 240 minutes is reduced by about 1.3 times as temperature increases from 308 to 318 K. The model simulated curves fitted well with the experimental curves. The mass transfer of the extraction process was studied by the mass transfer coefficients in Table 2. As solvent density decreases, the distance between the molecules of solute and extraction fluid decreases.
increased and became further apart, leading to an increase in mass transfer resistance in the fluid phase and solid phase. Consequently, this resulted in a reduced $k_{Ya}$ and $k_{Xa}$ values at higher temperatures.

### 3.2.3 Effect of CO2 flow rate

Figure 4 shows the influence of flow rate on the extraction of patchouli oil as a function of time, whereas Figure 5 shows the influence of flow rate as a function of solvent to feed ratio on particles of diameters between 0.3 and 0.6 mm, at operating pressure of 12 MPa and temperature of 313 K. The cumulative weight of oil improved at higher flow rates. There is no change to the physical properties, specifically density, of the supercritical CO2 when flow rate is varied. However, steeper slopes of the OEC at higher flow rates were observed in Figure 4 due to a greater amount of fresh solvent passing through the matrix. Since the driving force of the dissolution of solute from the matrix into the fluid is the concentration gradient from the solids to the extraction fluid, a faster flow rate will give a faster extraction rate, particularly in the early part of the extraction where the analyte concentration is the highest. Furthermore, a substantial flow rate is required to overcome mass transfer resistance as at low flow rates, the mass transfer resistance limits the amount of solute transported into the bulk of the solvent.

However, an excessively high flow rate would reduce residence time and cause the system to deviate from equilibrium. As a consequence, the fluid exiting the extractor would not have reached saturation. The amount of solvent that is in excess required to penetrate the cellular structure of the leaves simply bypassed the matrix because of intraparticle diffusion resistance. This effect is highlighted in Figure 5 by the smaller slopes of the OEC at higher flow rates.

Table 3 shows that, at higher flow rates, the mass transfer coefficient in the fluid phase ($k_{Ya}$) improved significantly due to enhanced mass transfer by convection in the higher amount of fresh CO2 passing through the packed bed. In addition, at higher flow rates, there was a decrease in the film thickness around the solid particles and hence a decrease in mass transfer resistance as represented by improved mass transfer coefficients in the solid phase ($k_{Xa}$).
FIGURE 4  Experimental and modeled curves (weight of oil vs time) at different CO₂ flow rates (P: 12 MPa; T: 313 K; dₚ: 0.3-0.6 mm)

FIGURE 5  Experimental curves (weight of oil vs solvent to feed ratio) at different CO₂ flow rates (P: 12 MPa; T: 313 K; dₚ: 0.3-0.6 mm)

| Q (g s⁻¹) | 0.0833 | 0.1667 | 0.2500 |
|----------|--------|--------|--------|
| Y* (g/g CO₂) | 0.0061 | 0.0048 | 0.0038 |
| Z         | 1.900  | 1.413  | 2.735  |
| W         | 0.0066 | 0.0037 | 0.0031 |
| xₜ        | 0.0996 | 0.0952 | 0.0955 |
| tCER/60 (s) | 25.47  | 24.93  | 10.61  |
| tFER/60 (s) | 76.51  | 61.48  | 40.76  |
| kₕA × 10⁻³ (s⁻¹) | 1.037  | 1.542  | 4.477  |
| kₓA × 10⁻⁶ (s⁻¹) | 6.867  | 7.715  | 9.562  |
| AARD (%)    | 3.64   | 3.60   | 2.96   |

TABLE 3  Fitting parameters, mass transfer coefficients, and absolute average relative deviation of BICM applied at different flow rates

Abbreviations: AARD, absolute average relative deviation; BICM, broken and intact cell model.

3.2.4  Effect of particle size

The influence of particle size on the extraction of patchouli oil is investigated by keeping pressure, temperature, and flow rate at 12 MPa, 313 K, and 0.1667 g·s⁻¹, respectively. As shown in Figure 6, The particle size of 0.3 to 0.6 mm yield the highest cumulative weight of oil, followed by the smaller size of 0 to 0.15 mm, and, lastly, the larger size range of 0.84 to 1.19 mm. Firstly, as particle size decreased, the effective surface area to extraction increased. Hence, there was more exposure and contact with the fluid allowing a better extraction rate. Secondly, grinding to a smaller particle size disrupts the cell walls and other inner barriers to mass transfer, subsequently liberating more accessible compounds to the solvent.³⁴,³⁵ Additional broken cells provided larger portions of easily accessible solute. Therefore, mass transfer
resistances in the fluid and solid phases decreased when particle size was reduced to 0.3-0.6 mm, as shown by the mass transfer coefficients in Table 4. However, when particles are excessively milled, the bed of particles was tightly packed, leading to nonhomogenous fluid flow through the bed. Small particle size may cause the fine powders to agglomerate, which could lead to longer diffusion paths and increased mass transfer resistances. In the study by del Valle, it was reported that the particle diameter has an effect on the optimal operational costs and extraction time. Particle size ranging from 0 to 0.15 mm was evaluated, and the results showed a decrease in extraction rate and mass transfer coefficients in the fluid and solid phases. Sabio et al. observed similar results where smaller particle size (0.08 mm) reduced the extraction yield obtained by SFE of lycopene and β-carotene from tomato processing waste.

4 | CONCLUSION

The effects of different operating process parameters, namely, pressure (9-15 MPa), temperature (308-318 K), solvent flow rate (0.0833-0.2500 g·s⁻¹), and particle size (0-0.15 mm, 0.3-0.6 mm, and 0.84-1.19 mm) on SFE of patchouli oil were investigated with experiments and mathematical modeling. BICM was used to model the mass transfer in the extraction process. The obtained mass transfer coefficients in the fluid phase and solid phase ranged from $1.04 \times 10^{-3}$ to $4.48 \times 10^{-3}$ s⁻¹ and $4.40 \times 10^{-6}$ to $1.40 \times 10^{-5}$ s⁻¹, respectively, indicating that convection mechanism is more representative than diffusion in the SFE of patchouli oil.

The density of supercritical CO₂ increased along with an increase in pressure, causing the mass transfer resistances in both the fluid and solid phases to decrease, which led to an improved extraction rate. In contrast, the increase in temperature had an opposite effect on the fluid density and mass transfer. An increase in supercritical CO₂ flow rate improved the driving force of dissolution of solute from the matrix into the fluid, hence overcoming mass transfer resistances in the fluid and solid phases. In terms of particle size, a moderate size between 0.3 and 0.6 mm provided optimal extraction and mass transfer as excessive grinding can lead to agglomeration and longer diffusion paths causing inhomogeneous extraction. In the case of patchouli oil extraction, the BICM predictions were in good agreement with experimental data, which

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**Table 4** Fitting parameters, mass transfer coefficients, and absolute average relative deviation of BICM applied at different particle size range

| $d_p$ (mm) | <0.3 | 0.3-0.6 | >0.6 |
|------------|------|---------|------|
| $Y^*$ (g/g CO₂) | 0.0046 | 0.0048 | 0.0043 |
| $Z$ | 0.8304 | 1.413 | 0.7232 |
| $W$ | 0.0022 | 0.0037 | 0.0017 |
| $x_k$ | 0.0963 | 0.0952 | 0.1024 |
| $t_{CER}/60$ (s) | 42.70 | 24.93 | 44.11 |
| $t_{FER}/60$ (s) | 79.00 | 61.48 | 76.67 |
| $k_{fr} \times 10^{-3}$ (s⁻¹) | 1.292 | 1.542 | 0.6977 |
| $k_{fr} \times 10^{-6}$ (s⁻¹) | 5.022 | 7.715 | 3.838 |
| AARD (%) | 4.96 | 3.60 | 5.53 |

Abbreviations: AARD, absolute average relative deviation; BICM, broken and intact cell model.
will be useful in future upscaling of such SFE processes. Furthermore, the BICM gave comprehensive knowledge of the mass transfer mechanism of the extraction process, including the mass transfer coefficients and the extraction periods governed by convection and diffusion. For further optimization and scale-up design, simulation and optimization tools such as simulator Aspen HYSYS™ can be used based on the extraction profile evaluated from experimental studies for evaluating techno-economic model of the process.\textsuperscript{38}

**ACKNOWLEDGEMENTS**

The authors are thankful for the laboratory facilities provided by Environmental and Water Technology Centre of Innovation and for financial support received from the Ministry of Education - Singapore through project MOE2015-TIF-2-G-051.

**CONFLICT OF INTEREST**

The authors have declared no conflict of interest.

| Symbols used                      |
|-----------------------------------|
| \(d_p\) [mm]  | Particle size               |
| \(k_{sa}\) [s\(^{-1}\)] | Mass transfer coefficient in the solid phase |
| \(k_{sv}\) [s\(^{-1}\)] | Mass transfer coefficient in the fluid phase |
| \(N\) [g] | Mass of nonextractable solid |
| \(P\) [MPa] | Operating pressure |
| \(Q\) [g\(\cdot\)s\(^{-1}\)] | Flow rate |
| \(t\) [s] | Time |
| \(T\) [K] | Operating temperature |
| \(W\) [-] | Parameter for slow extraction period |
| \(x\) [-] | Mass fraction of solute over nonextractable solid |
| \(Y^*\) [-] | Solubility of the extract in the fluid phase |
| \(Z\) [-] | Dimensionless coordinate |
| \(Z_w\) [-] | Parameter for second extraction period |

| Greek letters                      |
|-----------------------------------|
| \(\epsilon\) - | Bed porosity |
| \(\rho_{CO_2}\) [kg\(\cdot\)m\(^{-3}\)] | Density of the supercritical fluid |
| \(\rho_s\) [kg\(\cdot\)m\(^{-3}\)] | Density of the leaves |
| \(\rho_b\) [kg\(\cdot\)m\(^{-3}\)] | Bulk density |

| Subscripts                        |
|-----------------------------------|
| CER [-] | End of constant extraction rate |
| FER [-] | End of falling extraction rate |
| \(k\) [g] | Hardly accessible solute |
| \(o\) [g] | Total extractable solute in the matrix |
| \(p\) [g] | Easily accessible solute |

| Abbreviations                     |
|-----------------------------------|
| AARD [%] | Absolute average relative deviation |
| BICM [-] | Broken and intact cell model |
| CER [-] | Constant extraction rate |
| CO\(_2\) [-] | Carbon dioxide |
| FER [-] | Falling extraction rate |
| OEC [-] | Overall extraction curve |
| SFE [-] | Supercritical fluid extraction |

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**How to cite this article:** Soh SH, Agarwal S, Jain A, Lee LY, Chin SK, Jayaraman S. Mathematical modeling of mass transfer in supercritical fluid extraction of patchouli oil. *Engineering Reports*. 2019;1:e12051. [https://doi.org/10.1002/eng2.12051](https://doi.org/10.1002/eng2.12051)