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KINETIC MODEL IN DYNAMIC EXTRACTION OF *MOMORDICA CHARANTIA*

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ABSTRACT

Bitter gourd (*Momordica charantia*) which has been traditionally used in the treatment of type 2 diabetes mellitus (T2DM) was extracted using supercritical carbon dioxide (SC-CO_2). The SC-CO_2 is a fluid which possesses unique properties of high diffusivity and low viscosity. The aim of this study was to investigate the effect of different mean particle size in the determination of overall mass transfer coefficient using kinetic model of single sphere model (SSM) with the combination of simplified linear driving force model (LDFM). The mean particle sizes used were 0.20, 0.30, 0.50 and 0.70 mm using 1:3 feed-to-solvent ratio of ethanol as co-extractant at constant operating conditions (4 mL/min of SC-CO_2, 65 ^oC and 20 MPa). The results showed that mean particle size of 0.30 mm fit well in a kinetic model, SSM and simplified LDFM with the highest D_e value, i.e. 8.82 x 10^{-12} m^2/s. Furthermore, it shows a high mass transfer coefficient in fluid phase, k_f and overall, k_p value, i.e. 2.32 x 10^{-6} and 2.61 x 10^{-7} m/s respectively. Based on the results, it can be concluded that 0.30 mm is the best mean particle size to be used in the extraction of bitter gourd using SC-CO_2 solvent.

Keywords: Linear driving force model, *Momordica charantia*, particle size, single sphere model, supercritical carbon dioxide.

1.0 INTRODUCTION

Bitter gourd is scientifically known as *Momordica charantia* lies in *Cucurbitaceae* family. It is widely used to treat type 2 diabetes mellitus (T2DM) traditionally [1]. Referring to the data in Malaysia National Diabetes Registry volume 1 [2], 99.3% of the total registered diabetes patient is diagnosed with T2DM and out of this 58.4% women are in the age of 45 - 54 years. The T2DM disease is mainly due to insufficient insulin hormone produced in the pancreas to control the glucose level in the blood stream [3].

Previously, several conventional methods such as decoction, maceration, organic solvent extraction and etc have been used for extraction of bitter gourd. However, due to people's awareness on the toxic and hazardous of an organic solvent such as chloroform and dichloromethane, supercritical carbon dioxide (SC-CO_2) solvent has been used to extract the natural product as an alternative to the conventional method. The SC-CO_2 is a fluid with low viscosity and high diffusivity, therefore the fluid has better transport properties than liquid and easily diffuse into the solute particle which then enhanced the extraction rates [4]. The other advantages of using SC-CO_2 in the extraction of natural product are economical, nontoxic, non-flammable, inert and naturally abundant other than its relatively mild operating condition. Kinetic models such as single sphere model (SSM) and simplified linear driving force model (LDFM) are the simple model to describe the relationship between internal diffusion and mass transfer process of a single particle and supercritical solvent [5]. Therefore, the aim of this study was to investigate the effect of different mean particle size in intraparticle diffusion coefficient, D_e value using SSM as well as the determination of mass transfer coefficient by simplified LDFM.

2.0 MATERIALS AND METHOD

2.1 Materials

The green *Momordica charantia* fruits grown in Simpang Renggam (Johor, Malaysia) were purchased from a local market. The fruits were washed to eliminate any traces of impurities, cut into small pieces and dried in an oven (Memmert UFE 500) at 50^{o}C for 24 hours [6]. The dried sample was then grounded using commercial blender (Waring, U.S). The ground samples were sieved 0.2, 0.3, 0.5 and 0.7 mm mean particle size using Endecotts Octagon 2000 Digital Sieve Shaker. The sample was then stored in a tight seal container inside the freezer (-20^{o}C) until the extraction day.

Carbon dioxide (purity 99.99%) was procured from Kras Instrument & Service (Johor Bahru, Malaysia). Pure (100%) ethanol was purchased from Merck (Darmstadt, Germany).

2.2 Supercritical Carbon Dioxide (SC-CO_2) Extraction

The supercritical carbon dioxide extraction was carried out over 5 g of *Momordica charantia* sample mixed with 1:3 pure ethanol in an extractor vessel at constant pressure 20 MPa and temperature 65 ^{o}C using Supercritical Fluid Extraction (SFE) laboratory apparatus as shown in Figure 1, which consists of force ventilation oven (MMM Group, German) fitted with a 50 mL stainless steel extraction vessel. Pure 99.99% CO_2 gas (Kras Instrument & Service, Malaysia) was liquidized using a refrigerated bath circulator (Daihan Scientific. Co Ltd, Korea) and pumped to extraction vessel using carbon dioxide liquid pump (Tokyo, Japan) with a constant flow rate of 4 mL/min. The pressure in the extraction vessel was regulated by means of a back-pressure (Tescom Corp., U.S) valve installed in the line between the extraction vessel and the separator.

The depressurization process using control valve will convert the supercritical phase of carbon dioxide into its original phase with the help of water circulation bath (Daihan Scientific. Co Ltd, Korea) at the separator line which can separate the CO_2 from the extracted sample. The extraction process was done dynamically for total extraction time of 120 min and oil yields collected at every 15 min interval. The *Momordica charantia* extract was weighed using the analytical balance (Ohaus, U.S) with an accuracy up to 0.0001 g. The percentage of *Momordica charantia* extract yield was then calculated using Equation (1). The extract was later stored in a freezer (-20 ^{o}C) until further analysis.

$$\text{Extract yield (\%)} = \frac{\textit{Momordica charantia}\ \text{extract (g)}}{\text{Initial sample (g)}} \times 100 \qquad (1)$$

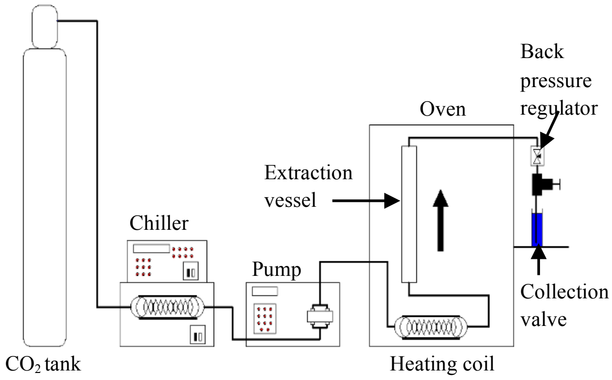

Figure 1 Supercritical carbon dioxide extraction schematic diagram

2.3 Single Sphere Model (SSM)

Single sphere model which also known as Crank model was used in order to investigate the effect of particle size in influencing the mass transfer of solute-solvent in the fixed bed under the supercritical condition. Crank [7] developed an equation to solve the diffusion in sphere when the surface concentration is maintained constant by substituting diffusivity, D with intraparticle diffusion coefficient, D_e [8].

The assumptions for the model are, the single sphere solid particle was assumed to be a "hot ball" with similar size in a constant medium. Then, the solute to be extracted was allocated uniformly inside the solid particle. Next, all solid particles were assumed to be at the same stage of extraction. The supercritical fluid flow rate was fast enough to penetrate inside the solid particle (mass transfer resistance close to zero). Lastly, intraparticle mass transfer was the controlling factor in the extraction process. More importantly, an axial dispersion is neglected in the extraction process.
The total amount of diffusing substance entering or leaving the sphere in non-steady state is given in Equation (2),

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_e n^2 \pi^2 t}{r^2} \right) \tag{2}$$

where, M_t (g) is the total amount of solute diffused from sphere at time, t (s), M_∞ (g) is the total amount of solute, n is the number of iterations, D_e (m^2/s) is the diffusion coefficient, r (m) is the particle radius range from $1\text{x}10^{-4} - 3.5\text{x}10^{-4}$ m based on the mean particle size studied in this work and t (s) is the extraction time. Solver in Microsoft Excel© 2013 was used to solve the equation.

2.4 Simplified Linear Driving Force Model (LDFM)

Bartle *et al.* [9] suggested that the rate of extraction is determined by the rate of mass transfer out of the matrix instead of solubility since the compound concentration in supercritical condition is below the solubility limit. Goto *et al.* [10] concluded that the overall mass transfer coefficient, k_p is a combination of external mass transfer, k_f and intraparticle diffusion coefficient, D_e based on parabolic profile assumption of linear driving force model as shown in Equation (3),

$$k_p = \frac{k_f}{1+\frac{Bi}{5}} \quad (3)$$

where, Biot number, $Bi=\frac{k_f.r}{D_e}$ as stated by Goto *et al.* [11]. The extraction process is said to be in the diffusion-controlled condition when the Biot number is more than 10.

Reverchon *et al.* [12] showed that the external mass transfer, k_f can be determined from Sherwood number if the value D_e is known for solute-solvent mass transfer in a supercritical condition as shown in Equation (4),

$$Sh= \frac{d_p k_f}{D_e} \quad (4)$$

where, d_p is particle diameter in unit m.

Wakao and Funazkri [13] proposed that the Sherwood number for Reynolds number in the range of 3 to 10,000 and Schmidt from 0.5 to 10,000 can be calculated using the corrected correlation as shown in Equation (5),

$$Sh=2+1.1Re^{0.6}Sc^{1/3} \quad (5)$$

where, $Re= \frac{\rho d_p v}{\mu}$, $Sc= \frac{\mu}{\rho D_e}$, ρ is density mixture in unit kg/m^3 based on Perry and Green [14], μ is viscosity mixture in unit kg/m.s based on Chung method [15] and v is interstitial fluid velocity in unit m/s.

2.5 Statistical Analysis

The deviation between the calculated and experimental value was evaluated. Model with the lowest amount of absolute average relative deviation (AARD) will be the best model to be used for further research. The AARD formula can be presented as Equation (6),

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{y_{calculated} - y_{experimental}}{y_{experimental}} \right| \times 100 \quad (6)$$

where, N is a total number of experimental data. While, $y_{calculated}$ and $y_{experimental}$ are the extract yield obtained from model equations and experiments, respectively at i condition.

3.0 RESULTS AND DISCUSSION

3.1 Determination of Intraparticle Diffusion Coefficient, D_e using SSM

In this section, the determination of intraparticle diffusion coefficient, D_e value using SSM is revealed for different mean particle size. Referring to equation of SSM, particle radius, r is directly proportional to the D_e value. Therefore, the effect of mean particle size is important in extraction process of *Momordica charantia*. Figure 2 shows the effect of mean particle size on *Momordica charantia* extract yield using SC-CO_2 extraction at constant parameter of pressure, i.e. 20 MPa, temperature i.e. 65 ^oC and SC-CO_2 flow rate, i.e. 4 mL/min. From the figure, it shows that the mean particle size of 0.30 mm imparted the highest yield and diffusion coefficient according to SSM curve in comparison with other mean particle sizes. Highest D_e value indicates that the solvent easily diffuses inside solid particle due to decrease in mass transfer resistance.

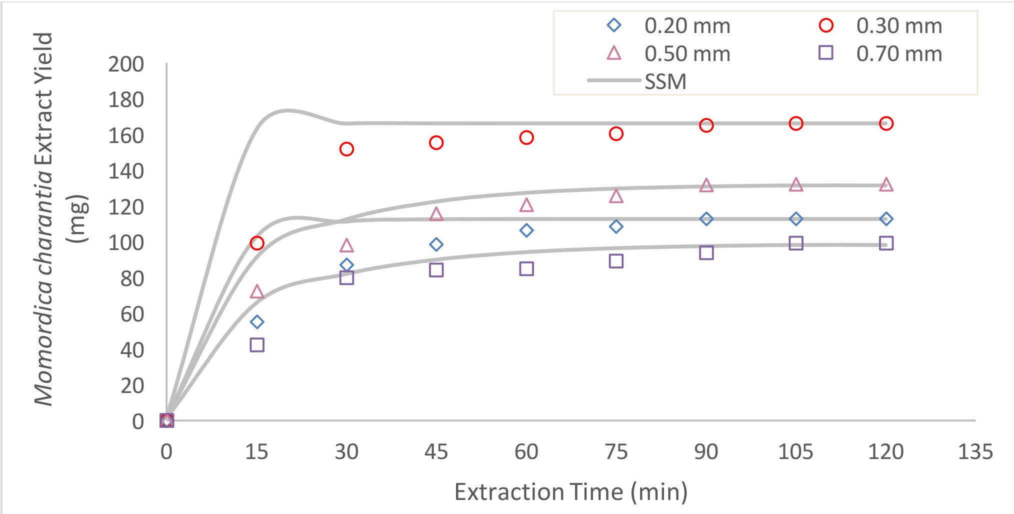

Figure 2 Effect of mean particle size on *Momordica charantia* extract yield using SC-CO_2 extraction at constant parameters (20 MPa, 65 ^oC and 4 mL/min)

Figure 2 shows that the extraction curve of 0.30 mm experimental data starts off with fast extraction phase where all the free solute on the solid surface easily dissolves in the solvent. Then, the extraction slows down after 30 min and enter the intermediate phase or transition phase. After that, the extraction reaches plateau phase or slow extraction phase at 90 min. At this phase, the internal diffusion takes place where the solvent penetrates deep inside solid particle to extract trapped solute in the solid particle's pore. Meanwhile, SSM predicted that the intermediate phase will starts after 15 min and then reach plateau phase for the rest of the extraction time. According to Yunus [16], the particle size influences the total extraction time if diffusion controlled the extraction process.

In addition, Table 1 summarized the D_e value and percentage of extract yield in the dynamic extraction of *Momordica charantia* at different mean particle size. The table shows that the smaller mean particle size of 0.30 mm imparted the highest yield, i.e. 166 mg and D_e value of 8.82 x10^{-12} m^2/s with AARD of 5.96%. Whereas larger mean particle size of 0.50 and 0.70 mm only obtained a relatively high D_e value, 7.45 and 8.69 x10^{-12} m^2/s respectively. On the other hand, the smallest mean particle size of 0.20 mm imparted the lowest amount of D_e value, 6.65 x10^{-12} m^2/s and the highest AARD of 7.71%. Vladić *et al.* [17], stated that the fitting model is acceptable when the AARD value up to 5~10% only. Above 10% indicates poor correlation between experimental data and fitted model.

Table 1 Summarize of intraparticle diffusion coefficient, D_e and extract yield for different mean particle size, d_p at 20 MPa, 65 ^oC and 4 mL/min in SC-CO_2 with 1:3 ethanol as co-extractant

Mean Particle Size, d_p (mm)	Diffusion Coefficient, D_e x10^{12} (m^2/s)	Extract Yield (mg)	AARD (%)
0.20	6.65	113	7.71
0.30	8.82	166	5.97
0.50	7.45	132	6.07
0.70	8.69	99	5.95

The reason that mean particle size of 0.3 mm could imparted the highest extract yield and D_e value is due to its larger surface area which shortens the diffusion path of solute-solvent to travel. Therefore, it is easier for the SC-CO_2 solvent to diffuse into and out of the *Momordica charantia* solid particle. However, for the mean particle size of 0.20 mm, the D_e value and the amount of extract yield are decreases due to increase in mass transfer resistance inside the solid phase. Besides, the channelling phenomenon where the solid particle is too fine and thus form a cake inside the extractor vessel which restrict the penetration of solvent into the solid particle. Hence, the solvent can only dissolve free solute on the solid surface. In comparison, larger mean particle size such as 0.50 have smaller surface area consequently increase the mass transfer resistance thereby decreasing the D_e value and extract yield. Furthermore, the largest mean particle size of 0.70 mm imparted the lowest amount of extract yield, i.e. 99 mg even though its imparted a higher D_e value according to SSM. The reason could be explained based on the Equation (2) where the particle radius and total extract yield are the major influences in the determination of D_e value. According to SSM, the larger particle radius and higher total yield will eventually increase the D_e value. Though in principle, the larger particle size have smaller surface area which restrict the solute-solvent contact and thus decrease the extract yield. Silva and Delgado [18] found that particle size is the most influence parameter in the diffusion coefficient in their study. They observed that the models used, deviate significantly from the experimental data in different particle size studied. Indeed, particle size will influence the diffusion coefficient in the extraction process. Thus, SSM has successfully predicted D_e value for different mean particle size in this study.

3.2 Mass Transfer Coefficient by Simplified LDFM

The overall mass transfer coefficient, k_p and mass transfer coefficient in the fluid phase, k_f were determined by simplified LDFM after obtained the D_e value from SSM. As explained by Mohd Nasir *et al.* [5], k_f and k_p value have direct connection with D_e value. Table 2 shows the mass transfer coefficient for different mean particle size. From Table 2, mass transfer in the fluid phase, k_f and overall mass transfer coefficient, k_p decreases as the mean particle size increase. Mean particle size of 0.20 mm shows the highest k_f and k_p value, i.e. 2.65 x 10^{-6} and 2.95 x 10^{-7} m/s respectively in comparison with other mean particle sizes. Hence, it indicates that higher amount of solute has been transferred especially in fluid phase due to its larger surface area. Similarly, the mean particle size of 0.30 mm also shows a high k_f and k_p value, i.e. 2.32 x 10^{-6} and 2.61 x 10^{-7} m/s respectively.

Table 2 Mass transfer coefficient for different mean particle size, d_p at constant parameters (20 MPa, 65 ^oC, 4 mL/min of $SC\text{-}CO_2$ with 1:3 ethanol as co-extractant, $\mu = 1.64x10^{-5}$ kg/m.s)

d_p (mm)	v x 10^3 (m/s)	*Re*	*Sc*	*Sh*	*Bi*	k_f x 10^6 (m/s)	k_p x 10^7 (m/s)
0.20	1.52	12.91	3548	80	40	2.65	2.95
0.30	1.16	14.81	2675	79	39	2.32	2.61
0.50	0.95	20.10	3168	100	50	1.49	1.35
0.70	0.76	22.43	2715	101	51	1.26	1.13

Viscosity mixture (μ), interstitial fluid velocity (v), Reynolds number (*Re*), Schmidt number (*Sc*), Sherwood number (*Sh*), Biot number (*Bi*), mass transfer coefficient in the fluid phase (*kf*), overall mass transfer coefficient (*kp*).

On the other hand, both larger mean particle sizes, i.e. 0.50 and 0.70 mm have smaller amount of k_f and k_p value indicates the increase in mass transfer resistance within solid particle and fluid phase as well as the smaller surface area for solute-solvent contact. Samadi and Vaziri [19] suggest that the larger particle size decrease the diffusivity of the solvent to dissolve the solute, due to the smaller surface contact and high mass transfer resistance surround the solute which leads to the importance of optimal particle size in the system. Therefore, it can be concluded that smaller mean particle size is the best particle size for the extraction of *Momordica charantia* using $SC\text{-}CO_2$.

4.0 CONCLUSION

In this study, it showed that mean particle size of 0.30 mm fit well in a kinetic model, SSM and simplified LDFM with the highest D_e value, i.e. 8.82 x 10^{-12} m^2/s. Furthermore, it shows a high mass transfer coefficient in k_f and k_p value, i.e. 2.32 x 10^{-6} and 2.61 x 10^{-7} m/s respectively. Hence, it explains the higher amount of *Momordica charantia* extract yield in comparison with other mean particle sizes. Based on the results, it can be concluded that 0.30 mm is the best mean particle size to be used in the extraction of *Momordica charantia* using $SC\text{-}CO_2$ solvent due to its high diffusivity in the solvent and lower mass transfer resistance for efficient solute-solvent contact.

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