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Research paper

Solubility Modelling pf Butterfly Wing Leaves (*Christia Vespertilionis*) in Supercritical Carbon Dioxide

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Abstract

Medicinal herb *Christia vespertilionis* oil has been claimed to possess anti-cancer and anti-plasmodial properties and show interest in food and pharmaceutical industries. Being an important alternative medicine plant, solubility data of *Christia vespertilionis* oil is demanded in order to understand the separation process and is crucial for designing purposes. In this work, extraction and determination of the oil's solubility were carried out using a green technique of supercritical carbon dioxide at a temperature range of 40 to 60℃ and 276 to 414 bar of pressure. The results demonstrated that the highest solubility was obtained at the highest temperature and pressure of 60℃ and 414 bar, respectively. For solubility prediction, experimental data were modelled using four empirical density-based models: Chrastil, del Valle and Aguilera, Adachi and Lu, and Sparks et al. models. In general, all the models were able to predict the solubility of *Christia vespertilionis* oil in supercritical carbon dioxide. The best fitting showed that Adachi and Lu model gave the best correlation with the lowest %AARD value of 1.61%.

Keywords: *Christia vespertilionis; correlation; density-based models; solubility; supercritical fluid extraction*

1. Introduction

Medicinal herbs have been widely consumed by most people as complementary and alternative medicines as they provide important pharmaceutical characteristic with no side effect to human body. Recently, one of the plant herbs that received increasing public attention due to its medicinal properties used to treat several critical diseases is known as *Christia vespertilionis* (L.) Bakh. from Fabaceae family. The plant is locally known as butterfly wing due to its shape that is similar to the wing of a butterfly. The medicinal benefit of the *C. vespertilionis* plant has been studied by numeral researchers where they found that it contains anti-proliferative potential for neuroendocrine tumour [1], anti-plasmodial activity for malaria disease [2], [3] and as tumor-inhibitor when tested on a mouse [4]. Since ancient times, the *C. vespertilionis* plant was consumed as traditional treatment in healing snakebites, tuberculosis, bronchitis, colds, muscle weakness, poor blood circulation [5], fever treatment [6] and healing scabies disease [7].
To-date, all extraction studies on the *C. vespertilionis* were conducted using conventional organic solvent extraction. However, this technique is not suitable and not safe for edible products. Major drawbacks of solvent extraction include compound degradation, product impurities, extensive extraction time, exposure of toxic to surrounding and pollute the environment [8]. Therefore, a green separation technology using supercritical carbon dioxide (SC-CO_2) fluid is introduced in this study to overcome the issues. Application of supercritical fluid extraction has received attention as a promising green extraction technique because it is free from any of toxic solvent residues which makes it suitable for separation of phytocompounds from natural foods and plants. In principle, carbon dioxide (CO_2) becomes supercritical fluid when it is heated and pressurised above its critical temperature of 31.1℃ and critical pressure of 73.8 bar. The use of CO_2 as supercritical fluid is ideal for extraction of functional foods and medicines since it is known to be nontoxic, noncorrosive, inert and safer to consumer and environment [9]. Other advantages by SC-CO_2 include fast extraction time, mild operating temperature, organic solvent-free and clean extract produced.
In SC-CO_2 process, the knowledge of solute solubility is vital and must be modelled for the effectiveness of process design such as extractors, separators, transfer lines, valves and process controllers [10]. Numerous solubility models have been proposed as prediction tools for SC-CO_2 extraction process where it could save energy, time and cost of operation. The models are classified as theoretical equations of state and density-based approach [11]. Due to simplicity of the application, the density-based models were widely implemented for solubility modelling where the models only need available independent variables such as pressure, temperature and density of pure fluids [12]. To-date, no reported work was found on the solubility behaviour of *C. vespertilionis* oil using green SC-CO_2 extraction. Thus, this work focused on the extraction of *C. vespertilionis* using SC-CO_2 method at various temperatures and pressures. The aims of this study are to determine the solubility of *C. vespertilionis* oil in SC-CO_2 and to determine the best solubility model to fit the solubility data of *C. vespertilionis* using four empirical density-based models such as Chrastil, del Valle and Aguilera, Adachi and Lu, and Sparks et al. models.

2. Experimental

2.1. Materials and Sample Preparation Method

Leaves of fresh plant of *Christia vespertilionis* were purchased from Pure Rerama Leaf which was located in Bukit Subang, Malaysia. Only the green leaves were selected in this study. Carbon dioxide (CO_2) with purity of 99.99% used in supercritical fluid extraction was purchased from Air Liquide in Singapore. Samples were oven-dried at temperature of 40°C for 24 hours to a final moisture content of 8 wt% on a wet basis. Dried samples were then ground using Waring Laboratory Blender and sieved through Endecotts Octagon 2000 Digital Sieve Shaker to obtain an average particle size of 0.3 mm.

2.2. Supercritical Carbon Dioxide Extraction

SC-CO_2 extraction was performed by using SFT-100 from Supercritical Fluid Technologies, Inc. (USA). CO_2 liquid tank for the SFT-100 contained 99.99% of CO_2 purity with a long dip tube and 55 - 62 bar of tank pressure. About 5 g of powdered *C. vespertilionis* was inserted into an extraction bag and placed in a 25 mL of pressurized vessel. Then, the pressure vessel was sealed tightly to ensure that there is no leakage. A high pressure of liquid CO_2 was pumped into the extractor and regulated by a back-pressure regulator unit. The maximum pressure of the setup is 690 bar and maximum temperature is 150°C. In this work, various temperatures (40 to 60℃) and pressures (276 to 414 bar) were used to investigate their effect on solubility of *C. vespertilionis* oil in SC-CO_2 at constant flowrate of 24 mL/min and extraction time of 40 minutes. The extraction temperature and pressure used in this study has been chosen according to the previous literatures where the range used were from 40 to 60℃ of temperature and 200 to 414 bar of pressure has successfully been used for extraction of phytocompounds from plant materials [13], [14]. Once the system has been set to certain time, temperature and pressure, a dynamic valve was gently open to allow continuous flow of SC-CO_2 fluid. In this study, a combination of static and dynamic technique was used to determine the solubility of the *C. vespertilionis* oil in SC-CO_2 with a 10 minute of static soaking time, followed by a 10 minute of dynamic interval. The desired flowrate of SC-CO_2 through the sample was achieved by opening the restrictor valve slowly at 5 mL/min. The extracted oil was collected gravimetrically by placing a glass vial at the outlet of the restrictor and the CO_2 was decompressed into atmospheric pressure. The amount of extracted oil was weighed by using analytical balance Model Mettler Toledo AB204-S with an accuracy of 0.0001 g. The extraction was conducted in duplicate at identical operating conditions and the average value with standard error was used for solubility determination. In this work, the experimental solubility was determined from the slope of the graph of mass of extracted oil (mg) to the mass of CO_2 consumed (g) [15].

2.3. Solubility Modelling Using Empirical Models

The experimental solubility of *C. vespertilionis* oil in SC-CO_2 was fitted using four empirical of density based-models such as Chrastil (1982), del Valle and Aguilera (1988), Adachi and Lu (1983) and Sparks, Hernandez and Estévez (2008) as shown in Table 1. It is assumed that the oil extract was present as a single component in the determination on solubility of oil in supercritical fluid [20]. Chrastil model has been widely used to correlate the experimental data of solubility in pure SC-CO_2 fluid. The model was derived based on thermodynamic relationship between the solubility of solute and the supercritical fluid solvent with an assumption that equilibrium between solvated-complex of solute and solvent molecules has been reached. According to Table 1, S is solubility of oil in SC-CO_2 (kg/m^3), ρ is density of CO_2 (kg/m^3), T is extraction temperature (K), k is association number which represents number of supercritical fluid molecules in the solvated complex, a is a function of enthalpy of solvation and enthalpy of vaporization and b is solutes that had been extracted and depends on molecular weight and the melting point of the solute.

Table 1: Empirical Models for Solubility Correlation

Model	Model's Equation	
Chrastil (1982)	$S=\rho^{k}\exp\left(\frac{a}{T}+b\right)$	**(1)**
del Valle and Aguilera (1988)	$S=\rho^{k}\exp\left(\frac{a}{T}+\frac{c}{T^{2}}+b\right)$	**(2)**
Adachi and Lu (1983)	$S=\rho^{(k+d\rho+e\rho^{2})}\exp\left(\frac{a}{T}+b\right)$	**(3)**
Sparks et al. (2008)	$S=\rho^{(k+d\rho+e\rho^{2})}\exp\left(\frac{a}{T}+\frac{c}{T^{2}}+b\right)$	**(4)**

Since the Chrastil model has its own limitation where it is only applicable for the solubility within the range of 100 to 200 kg/m^3, a modification was proposed by del Valle and Aguilera [17]. The modification considered the enthalpy change of vaporisation with temperature with c as the new constant added to the original Charstil model. However, Adachi and Lu [18] change the value of k to a second order polynomial of the supercritical fluid density where d and e were added as the new parameters. They argued that in the application of Chrastil model the density plays an important role towards solubility. Thus, the association number, $\underline{k}$ must be a function of density i.e. $\underline{k}=k+d\rho+e\rho^2$. As studied by Sparks et al. [19], the modification of Chrastil model made by del Valle and Aguilera, and Adachi and Lu indeed has improved the performance of Chrastil model. However, several cases exist where one modification resulted to be better than the other and vice versa. Therefore, Sparks et al. [19] proposed a new modification by combining both considerations by del Valle and Aguilera, and Adachi and Lu. In this work, the logarithm graphs of models i.e. lnS against lnρ were plotted to determine the constant parameters by fitting the experimental data using a least squares method and curve-fitting approach computed by Microsoft Excel Solver programme. The accuracy of the models was determined by calculating the percentage of average absolute relative deviation (%AARD) as in Equation (5) where n is number of experimental points, S_{calc} is calculated solubility using the model and S_{exp} is the experimental solubility. The best correlation was decided based on the minimum %AARD obtained. To determine the reliability of the model used, a statistical analysis was performed using a Paired Samples T-test method in a Statistical Product and Service Solutions (SPSS) software.

$$AARD(\%)=\frac{1}{n}\sum\frac{\left|S_{calc}-S_{\exp}\right|}{S_{\exp}}\times 100 \qquad (5)$$

3. Results and Discussions

3.1. Experimental Data of Solubility

The solubility behaviour of *C. vespertilionis* oil at specific ranges of pressures and temperatures are presented in Figure 1 and Figure 2. As can be seen, the solubility increases as the pressure increased from 276 to 414 bar at all isothermal conditions. The solubility is the highest i.e. 0.167 ± 0.01 mg oil/g CO_2 when the pressure reaches 414 bar at constant temperature of 60℃. The increase of pressure by 138 bar from 276 to 414 bar has positively enhanced the oil's solubility to 0.167 ± 0.01 mg oil/g CO_2. This finding corresponds to the fundamental knowledge of supercritical fluid extraction in which solubility becomes favourable at high pressure due to increment of fluid density. Intermolecular forces between solute-solvent molecules strengthen as the density increased which enhanced the solvent strength to dissolve more solutes. The result on the effect of pressure on solubility of *C. vespertilionis* oil through SC-CO_2 extraction is in agreement with studies conducted by other authors [13], [21].

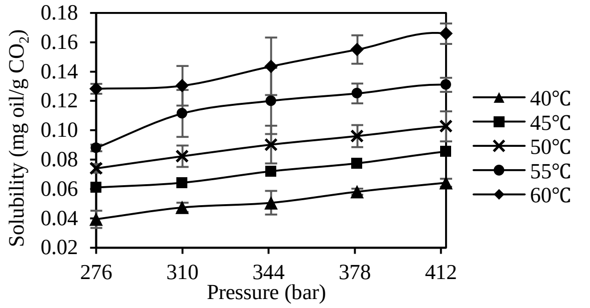

Fig. 1: Solubility of *C. vespertilionis* oil in SC-CO_2 versus pressure

A clear increment of solubility was illustrated in Figure 2 on the plotted graph of solubility of oil versus temperature. The increased of temperature by 5℃ from 40 to 60℃ has significantly increased the solubility in all isobaric conditions. The solubility was the highest when the temperature reached 60℃. The result revealed that at this temperature condition, the effect of vapour pressure was more dominant than the effect of the decreasing density. The increase of solubility also can be explained by the effect of CO_2 diffusion into the sample matrix at high temperature. Combination of increasing solutes vapour pressure and high diffusivity of the fluid has resulted in increased oil's solubility. Similar results were reported by several authors in their extraction of plant materials using the SC-CO_2 method [14], [22].

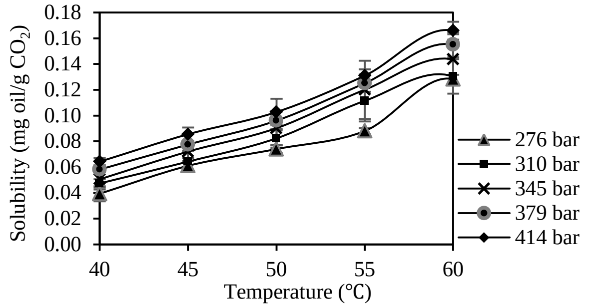

Fig. 2: Solubility of *C. vespertilionis* oil in SC-CO_2 versus temperature

3.2. Solubility Correlation Using Empirical Models

Figure 3(a) to Figure 3(d) show logarithmic relationship between solubility of *C. vespertilionis* oil in SC-CO_2 and density of pure SC-CO_2 of the empirical models used i.e. Chrastil, del Valle and Aguilera, Adachi and Lu, and Sparks et al. models. In general, a similar pattern of results by all models were observed. The adjustable parameters obtained from each model with %AARD values are presented in Table 2. As can be seen, the values of k were in the range of 4.000 to 4.630 which describes about four molecules of CO_2 have clustered a single molecule of *C. vespertilionis* oil in forming the solvated complex at equilibrium condition. On the other hand, for the parameter a, the values were found in the range between -6759.09 to -7023.93, with the negative value indicates that the energy was released during the formation of temporary bond when the extraction mechanism occurred [16]. Meanwhile, the range of parameter b for all models in which the solute was extracted was between -7.923 to -11.396.

Based on the result obtained, Adachi and Lu model showed the best correlation with the lowest of %AARD i.e. 1.61%. Adachi and Lu [18] modified the model in a way that the value of k should be of density-dependent since density of the supercritical fluid plays a very important role towards solubility. However, the %AARD for Chrastil and Sparks et al. models were found similar to the Adachi and Lu model i.e. 1.62% and 1.63% respectively. This indicates that the changes made by Sparks et al. [19] only provides limited improvement to the original Chrastil model. Among all the tested models, the del Valle and Aguilera model gave the highest %AARD of 2.17%. In general, the obtained results show that all density-based models are able to correlate the solubility of *C. vespertilionis* oil with low accuracy of %AARD achieved.

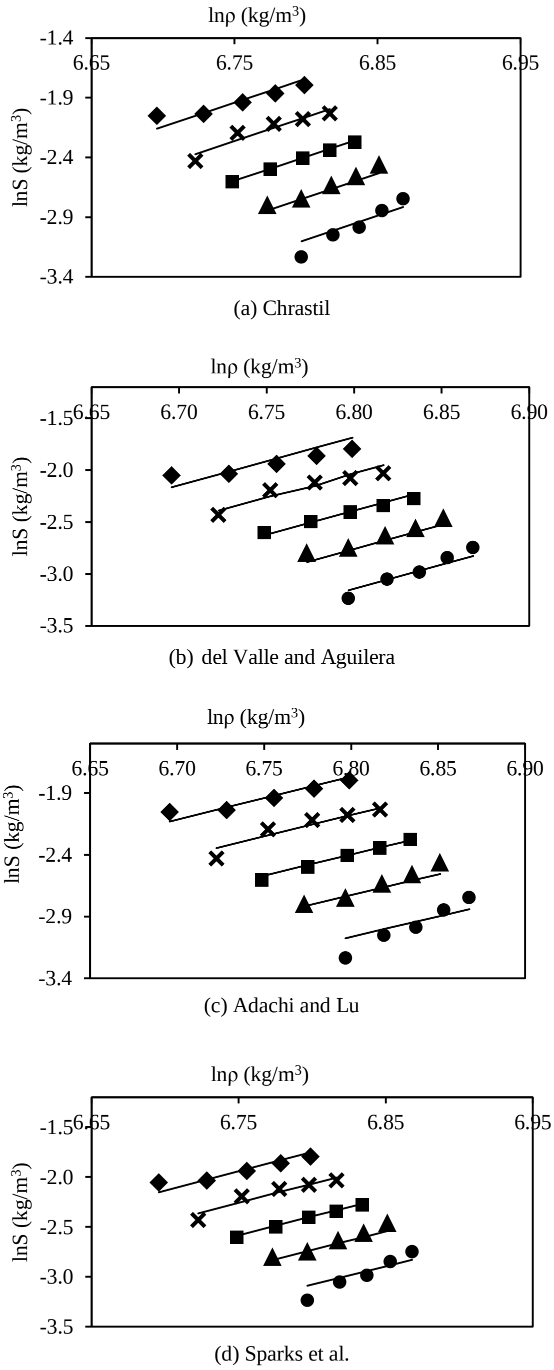

Fig. 3: Correlation of experimental solubility data with (a) Chrastil model, (b) del Valle and Aguilera model, (c) Adachi and Lu model, and (d) Sparks et al. model. Experimental solubility: ● =40℃, ▲ =45℃, ■ =50℃, **x** =55℃, ♦ =60℃, Predicted solubility: ___

Furthermore, the straight line obtained by the models indicate that the system obeys the model's theory. Table 3 shows the results from statistical analysis using SPSS software where it compares

Table 2: Adjustable Parameters of Empirical Models for *Christia vespertilionis* Oil in SC-CO_2

Model	k	a	b	c	d	e	%AARD
Chrastil	4.011	-7023.93	-7.923	-	-	-	1.62
del Valle & Aguilera	4.630	-6907.93	-11.396	-1.138 x 10^5	-	-	2.17
Adachi & Lu	4.000	-6759.09	-8.611	-	0.00008	-1.0 x 10^{-7}	1.61
Sparks et al.	4.001	-6921.09	-8.910	256.005	0.0003	-2.0 x 10^{-7}	1.63

the correlation coefficient (R^2), significance value (i.e. *p*-value), standard deviation and mean standard error between experimental solubility and the model. According to Table 3, the pair of experimental and calculated solubility using Adachi and Lu model showed a very high correlation with the R^2 value of 0.993. The Chrastil, del Valle and Aguilera, and Sparks et al. demonstrated a similar R^2 values that is higher than 0.98. The low value of standard deviation and mean standard error for all models has specified that the models are reliable to represent the solubility of *C. vespertilionis* oil in SC-CO_2 within the range of temperatures and pressures used in this study.

Table 3: Statistical Analysis using Paired Samples T-test

	Exp – Chrastil	Exp – del Valle & Aguilera	Exp - Adachi & Lu	Exp - Sparks et al.
Correlation coefficient (R^2)	0.992	0.989	0.993	0.992
Significance (p < 0.05)	0.000	0.000	0.000	0.000
Standard deviation	0.0047	0.0069	0.0043	0.0045
Mean standard error	0.000936	0.001375	0.000851	0.000907

4. Conclusion

The solubility of *C. vespertilionis* oil in SC-CO_2 fluid of 0.167 mg oil/ g CO_2 was found to be the highest value achieved at the highest temperature and pressure i.e. at 60℃ and 414 bar, respectively. Four empirical of density-based models were used as solubility correlation method of *C. vespertilionis* oil in the SC-CO_2 fluid. Among all tested models used, Adachi and Lu model demonstrated the lowest %AARD value of 1.61% which indicates that the model was well correlated with the experimental data within the range of experimental conditions. Solubility data of *C. vespertilionis* oil medicinal plant in SC-CO_2 is very important as it would contribute as new knowledge in supercritical fluid extraction area and may benefit other researchers in future development.

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