EXTRACTION AND MODELLING OF CATECHIN FROM *ARACHIS HYPOGEA* SKIN USING MODIFIED SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Peanut skin, which contains a high level of catechin, is removed as waste in peanut industry. Catechin is well-known for its antioxidant activity. In this study, modified supercritical carbon dioxide (SC-CO_2) extraction assisted by ethanol was performed to extract catechin from peanut skin. Modified SC-CO_2 extraction was carried out at various experimental conditions. The effects of pressure, temperature and ratio of modifier on the extraction yield, catechin and antioxidant activity were investigated by using the response surface methodology (RSM). Three established solubility models, including the Chrastil, the Del Valle Aguilera and Adachi Lu models were applied to describe the solubility behaviour. However, the formulation of a new solubility-based model is needed to adapt the presence of ethanol as a modifier. There were two new models, namely Well-Mix (W-M) and Unwell-Mix (U-M) models, proposed in this study with the assumption of significant solubility enhancement being promoted by the addition of ethanol. Furthermore, the capability of W-M and U-M models were examined by fitting the published solubility data of *Areca catechu*, Rosehips and Avocado seeds. The maximum extraction yield (15.34%), catechin concentration (156.40 $\mu g/g_{extract}$) antioxidant activity (95.99%) were obtained at 25.24 MPa, 60.83°C and 6.95 v/v% of modifier, respectively. It is proven that the effect of pressure and ratio of modifier were the significant factors required to achieve high yield extract, whereas the temperature and ratio of modifier effect gave the significant impact to obtain high catechin concentration and antioxidant activity. The W-M model offered the best fitting among all the models to correlate the solubility data of peanut skin extract with the lowest percentage of average absolute relative deviation (%AARD) of 4.20% and high coefficient of determination (R^2) of 0.976 achieved. The coefficient values of $k_{1(CO_2)}$ and $k_{2(Et-OH)}$ were 0.716 and 0.076, respectively. It is hence believed that the solvation power of SC-CO_2 was higher than ethanol to increase the solubility of peanut skin extract. Furthermore, the endothermic reaction was reported, where the solubility of solute increased with the temperature. It is also confirmed that the new models (W-M and U-M) demonstrate a good capability to fit the solubility data of *Areca catechu*, Rosehips and Avocado seeds as low average percentage of AARD (<15%) and high R^2 (> 0.8) were reported. The results of this study reveal that peanut skin is a potential source for pharmaceutical compounds and the new models could predict successfully the solubility of the solid solute in SC-CO_2 with the addition of modifier.

ABSTRAK

Kulit kacang yang mengandungi kandungan katekin yang tinggi, dibuang sebagai sisa dalam industri kacang. Katekin terkenal dengan aktiviti antioksidanya. Dalam kajian ini, pengekstrakan karbon dioksida superkritikal terubahsuai (SC-CO_2) berbantu etanol dilakukan untuk mengekstrak katekin daripada kulit kacang. Pengekstrakan SC-CO_2 terubahsuai dijalankan pada keadaan eksperimen yang pelbagai. Kesan tekanan, suhu dan nisbah pengubah suai terhadap hasil ekstrakan, katekin dan aktiviti antioksidan yang tinggi dikaji dengan menggunakan Kaedah Tindak balas Permukaan (RSM). Tiga model keterlarutan yang sudah mantap termasuk model Chrastil, Del Valle Aguilera dan Adachi Lu digunakan untuk menjelaskan tingkah laku keterlarutan. Walau bagaimanapun, rumusan model berasaskan kelarutan yang baharu diperlukan untuk menyesuaikan kehadiran etanol sebagai pengubah. Terdapat dua model baharu iaitu model Well-Mix (W-M) dan model Unwell-Mix (U-M), yang dicadangkan dalam kajian ini dengan andaian peningkatan keterlarutan yang ketara digalakkan dengan penambahan etanol. Selain itu, keupayaan model W-M dan U-M dikaji dengan memadankan data keterlarutan *Areca catechu*, biji Rosehips dan biji Avokado yang diterbitkan. Hasil pengekstrakan maksimum (15.34%), kepekatan katekin (156.40 µg / $g_{ekstrak}$) dan aktiviti antioksida (95.99%) masing-masing diperoleh pada 25.24 MPa, 60.83°C dan 6.95 v/v% pengubah suai. Telah terbukti bahawa kesan tekanan dan nisbah pengubah suai adalah faktor penting yang diperlukan untuk mencapai hasil ekstrak, sedangkan kesan suhu dan nisbah pengubah memberikan kesan yang ketara untuk mendapatkan kepekatan katekin tinggi dan aktiviti antioksidan. Model W-M menawarkan padanan terbaik di antara semua model untuk mengaitkan data keterlarutan ekstrak kulit kacang dengan peratusan rendah purata mutlak sisihan relatif (%AARD) pada 4.20% dan pekali penentuan (R^2) tinggi pada 0.976 yang diperoleh. Nilai pekali $k_{1(CO_2)}$ dan $k_{2(Et-OH)}$ masing-masing adalah 0.716 dan 0.076. Oleh itu, dipercayai bahawa kekuatan pensolvatan SC-CO_2 adalah lebih tinggi daripada etanol untuk peningkatan kelarutan kulit kacang. Tambahan pula, reaksi endotermik dilaporkan, dengan keterlarutan larutan meningkat dengan suhu. Disahkan juga bahawa model-model baharu (W-M dan U-M) menunjukkan keupayaan yang baik untuk menyesuaikan data keterlarutan *Areca catechu*, biji Rosehips dan biji Avokado sebagai purata rendah %AARD (<15%) dan R^2 tinggi (> 0.8) yang dilaporkan. Hasil kajian ini menunjukkan bahawa kulit kacang merupakan sumber yang berpotensi untuk sebatian farmaseutikal dan model baru dapat meramalkan kelarutan larutan pepejal dalam SC-CO_2 dengan tambahan pengubah suai dengan jayanya.

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LIST OF ABBREVIATIONS

AARD	-	Average absolute relative deviation
ABS	-	Absolute
A-L	-	Adachi-Lu
ANOVA	-	Analysis of variance
AH	-	Antioxidant
CO_2	-	Carbon dioxide
CER	-	Constant extraction rate
DPPH	-	2,2-Diphenyl-1-Picrylhydrazyl
DVa	-	Del Valle Aguilera
Et-OH	-	Ethanol
FER	-	Falling extraction rate
HPLC	-	High-performance liquid chromatography
O_2	-	Oxygen
QE	-	Quercetin
R·	-	Radical species
R^2	-	Coefficient of determination
RSM	-	Response surface methodology
RPM	-	Revolution per minute
SC-CO_2	-	Supercritical carbon dioxide
SFE	-	Supercritical fluid extraction
UV-Vis	-	Ultra-violet visible

LIST OF SYMBOLS

α	-	Alpha
NH_3	-	Ammonium
β	-	Beta
C	-	Critical point
P_c	-	Critical pressure
T_c	-	Critical temperature
^oC	-	Degree Celsius
d_1	-	Degree of freedom of regression
d_2	-	Degree of freedom of residue
δ	-	Delta
ρ	-	Density
D_e	-	Diffusivity of Coefficient, m^2/s
ft	-	Feet
γ	-	Gamma
g	-	gram
ΔH_{vap}	-	Heat of vaporisation
ΔH_{solv}	-	Heat of salvation
h/hr	-	Hour
ΔT	-	Increment of temperature
ΔP	-	Increment of pressure
Δt	-	Increment of time
K	-	Kelvin
Kg/h	-	Kilogram per hour
m_0	-	Mass in grams of dish
m_1	-	Mass in grams of dish and sample before drying
m_2	-	Mass in grams of dish and sample after drying
MPa	-	Mega Pascal
M_m	-	Micro meter
mL	-	millilitre
>	-	More than

nm	-	Nanometre
N_2	-	Nitrogen
N_2O	-	Nitrogen oxide
PPM	-	Part per million
%	-	Percentage
Y%	-	Percentage of overall oil yield
M_c%	-	Percentage of moisture content
psi	-	Pound per square inch
P	-	Probability
Y_i	-	Responses
k_1	-	Solvation power of supercritical carbon dioxide
k_2	-	Solvation power of ethanol
S	-	Solubility, g/mL
X_i	-	Variables
W-M	-	Well-Mix
$W_{extract}$	-	Weight of extract, g
wt%	-	Weight percentage
W_i	-	Weight of sample before extraction, g
W_f	-	Weight of sample after extraction, g
U-M	-	Unwell-Mix

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Peanut (*Arachis hypogaea*) is commonly grown in tropical and subtropical zones as a commodity that potentially supports farming economies of both small-scale holders and large-scale commercial producers. The global annual production of peanuts is reported to be 46 million tons per year on average. Peanut contains 21 to 36.4% of protein, 18% of carbohydrates and 36 to 54% fat (Bindhya and Anita, 2015). Peanuts are employed as raw materials in various food manufacturing industries, including peanut butter, roasted peanut snacks, peanut oil and peanut confections industries (Yu *et al.*, 2006). However, Peanut skin is usually removed as residue or by product before peanut consumptions to avoid astringent taste problem There is an average skin residue of 3% generated from peanut production annually (Elsorady and Ali, 2018). Peanut skin has low economic benefit and is commonly discarded or sold at low price for animal feed and plant fertilizer (Hoang *et al.*, 2008).

Many recent studies have confirmed that peanut skin contains a wide diversity of bioactive compounds such as phenolic acids, tocopherols and flavonols which remarkably possess food and pharmaceutical values (Franco *et al.,* 2018). One of the bioactive compounds presents in peanut skin is catechin. It is a type of flavanol, which possesses two benzene rings with five hydroxyl groups attached. Catechin is polar in nature due to its molecular structure. It exists abundantly in onion, cocoa, grape skin and tea. This is remarkably comparable with one of the notable catechin sources such as *Areca Catechu* and spearmints, which contains 0.0716 and 0.14 $mg_{catechin}/g_{sample}$, respectively (Bimakr *et al.*, 2011; Ruslan *et al.*, 2015). Catechin is recognized for its health benefits to human bodies including anti-inflammatory, anti-HIV, anti-depressant, and anti-hypertensive properties. It takes second place in exhibiting antioxidant activity in comparison with other natural antioxidant compounds (Katalinić *et al.*, 2004).

To date, conventional extraction methods such as maceration and Soxhlet extraction are used to extract peanut skin (Nepote *et al.*, 2002). Supercritical carbon dioxide (SC-CO_2) extraction is a modern and green technology to extract bioactive compounds from plants and herbs as it eases the public worry about the presence of toxic solvent for consumption. This extraction process uses non-toxic solvent (CO_2) and operates at low temperature which helps to prevent the degradation of thermo labile compounds. The key feature of SC-CO_2 extraction is the ability of manipulating the dissolving power of CO_2 towards targeted compounds by the appropriate selection of pressure and temperature. SC-CO_2 extraction also offers the major advantage in term of producing high purity and high selectivity extract.

SC-CO_2 has the limitation of interest compounds, where it is superb for non-polar compounds. However, it is quite challenging for extraction of polar compounds such as catechin. Therefore, modification of SC-CO_2 is needed to break the limitation of the interest compounds. Addition of ethanol is one of the modifications of SC-CO_2 where ethanol can enhance the polarity of SC-CO_2 to extract the polar compounds. Hence, modified SC-CO_2 extraction with additional of modifier is a promising technique for extraction of catechin as polar compound. Furthermore, the reason of choosing ethanol as modifier is that food grade ethanol is available in the market compared to others organic solvents commonly such as n-Hexane, acetone, methane and ethane.

It is often impossible to determine the solute solubility behaviour experimentally. Many empirical models are often used to overcome this constraint due to their application simplicity as it does not utilize physicochemical properties such as critical properties, acentric factor and sublimation pressure. There are three types of well-known empirical models, namely Chrastil (Chrastil, 1982), Del Valle Aguilera (DVa) (Valle and Aguilera, 1988) and Adachi Lu (A-L) (Adachi and Lu, 1983) models, which are commonly employed to predict the solubility behaviour of the solute. Chrastil model is developed based on the solvato-complex of the interaction between the solute and SC-CO_2 (Chrastil, 1982). The DVa model is meanwhile the modified Chrastil's equation with the assumption by which temperature gives significant impact to encourage the solubility. On the other hand, A-L model is derived with the assumption claiming that density of CO_2 is the significant parameter to enhance the solubility of solute. Therefore, there are least studies that the empirical models consider the effect of polar modifier as one of the significant parameters to enhance the solubility of solute.

1.2 Problem Statement

Valorisation of catechin rich peanut skin, as a potential natural source of antioxidants, from low value material can be economically attractive for the future food and pharmaceutical industries. There are currently many established extraction technologies used to retrieve bioactive compounds from plants and herbs. Solvent extraction using alcohol is the most common extraction method used. However, it has the major drawbacks like long extraction time, high consumption of toxic solvent, low extraction selectivity and decomposition of heat sensitive compounds. To overcome the mentioned limitations, SC-CO_2 extraction is one of the promising alternatives that offers the high quality of extract production. CO_2 is non-polar in nature, which make it an outstanding green solvent to extract non-polar compounds but not for polar compounds. The addition of a small amount of ethanol could significantly enhance the both extract yield and catechin with high antioxidant activity extract by improving the polarity of CO_2. There are several parameters, such as temperature, pressure, flowrate of CO_2, presence of modifier, extraction time, particle size and moisture content of feed, that affecting the yield and quality of extract. Therefore, the identification of the most affecting factors and the best operating condition to maximize the extract yield and quality should be conducted.

In SC-CO_2 extraction process, the feasibility of the extraction process can be evaluated by predicting the solubility behaviour of the interested solute using the well-known solubility models. However, the established models fail to accurately correlate the solubility data involving two different solvents as these models usually neglect the presence of modifier. Hence, the formulation of the new solubility model is proposed in this study. The coefficient value generated from the new model can be employed to determine the solvation power of SC-CO_2 and ethanol. The dominant solvent can hence be identified.

1.3 Research Objectives

The objectives of this study are:

i. To determine the optimum operating conditions on the high yield, catechin and antioxidant activity from peanut skin by modified SC-CO_2 extraction.

ii. To develop new solubility models for SC-CO_2 extraction and comparison with the established solubility models.

iii. To evaluate the capability of new models to fit solubility of plants extract in SC-CO_2.

1.4 Scopes of the Study

The scopes of this study include:

i. Preliminary studies were needed to fix the selected variables. The preliminary operating conditions of extraction were pressure (10 and 30 MPa), temperature (40 and 70 °C) and the flow rate of carbon dioxide (2 to 4 mL/min) with 4 hours extraction time.

ii. The quantification of catechin was determined using High-Performance Liquid Chromatography (HPLC) by overlaying the peak area obtained with the catechin standard.

iii. Antioxidant activities of the extract were analysed by using 2,2-Diphenyl-1- picrylhydrazyl (DPPH) method.

iv. The operating conditions for extraction were pressure (10 to 30 MPa), temperature (40 to 70 °C) and the ratio of modifier (2.5 to 7.5%). Response surface methodology is used to determine the best condition and the most significant parameters.

v. The result of multiple response optimisation of the peanut skin extraction was compared by Soxhlet extraction with different solvents such as ethanol, water and n-hexane in term of the yield extract, antioxidant activity and catechin concentration. The temperature condition was based on the boiling temperature point of each solvent.

vi. Formulation of new density-based model was developed from Chrastil model. The main assumption was the final product extraction was homogeneous or heterogeneous phase. Therefore, the coefficient values of new models were established to determine the solubility behaviour.

vii. The new models were compared with other established solubility models (DVa, Chrastil and Adachi Lu). The best fitting of solubility data was based on the low percentage of average absolute relative deviation (%AARD) and high coefficient of determination (R^2).

viii. The proposed new models were applied to fit another established solubility data of plants (*Areca catechu*, avocado seeds and rosehips seeds). The new models were evaluated based on the (%AARD) and (R^2) between solubility data and the model to determine the capability of the new models fitted another solubility plant extract

1.5 Significance of Study

There are two critical points in the significance of the study. First, the optimum conditions of modified SC-CO_2 to obtain the high yield, catechin and antioxidant activity. Furthermore, the two new models are established through this study to determine the solubility behaviour of plant extract in SC-CO_2 and ethanol. Besides, the models can examine the solvation power of SC-CO_2 and ethanol in the extraction process. Therefore, the dominance of solvents between SC-CO_2 and ethanol can be determined.

1.6 Limitations of the Study

The limitation of this study is that the maximum operating pressure has been restricted to 30 MPa, while the temperature was 70 ºC. Although, the melting point of catechin is 175 °C, the catechin will degrade at temperature 70 °C (Ruslan *et al.*, 2018). This is due to the thermo labile effect of catechin. Yesil-Celiktas *et al.* (2008) also found that degradation in catechin was observed when treated at 80 °C. Furthermore, the ratio of modifier was restricted to 7.5% due to the prevention the changing supercritical phase to subcritical phase (Machmudah *et al.*, 2006).

1.7 Thesis Outline

This thesis is organised in five chapters. Chapter 1 begins with the introduction of this research project along with a brief introduction of supercritical fluid extraction, catechin as the bioactive compound of *Arachis hyphogea* skin and various models. This chapter also includes the problem statements that motivated this research, the objectives, scopes and significance of this research.

Chapter 2 presents an overview of the pharmacology properties of the peanut (*Arachis hyphogea*) skin. This chapter also describes the fundamental theory of supercritical fluid extraction, chemical and physical properties. It also presents the selection of extraction conditions and solvents, and a review of the previous research related to the topic of interest. The response surface methodology (RSM) and modelling of SC-CO_2 extraction are also reviewed in this chapter.

Chapter 3 describes the detailed methodology to achieve the research objectives. The experimental work for the extraction process, compound analysis and biological analysis are mentioned as a guideline for this research. The design of experiments is also presented in this chapter. The explanation of the formulation of the new solubility model is also explained in this chapter.

Chapter 4 is discussed in two different parts. The first part presented the findings through experimental work including the effects of operating conditions on the extracted yield and catechin concentration. The mathematical models of solubility behaviour are discussed in the latter part.

Finally, Chapter 5 highlights the conclusions and recommendations of the work. The conclusions are summarised based on the results and discussion in Chapter 4. The recommendations presented suggest guidance and improvement for future work related to the modified SC-CO_2 extraction and peanut skin.

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