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RESEARCH ARTICLE

Diffusivity optimization of supercritical carbon dioxide extraction with co-solvent-ethanol from peanut skin

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Abstract

Peanut skin is a waste of industrial peanut butter that contains bioactive compound, which is used as antioxidant, anti-diabetic, anti-cancer, and anti-inflammatory. Supercritical carbon dioxide (SC-CO_2) extraction as green technology is applied to extract peanut skin oil. The aim of this study is to optimize the operational conditions of pressure, temperature, and percentage of co-solvent to obtain oil yield and diffusivity coefficient. Determination of diffusivity coefficient was needed to evaluate the mass transfer between solvent and solute. The operational conditions of SC-CO_2 studied were different pressure (10, 20, 30 MPa), different temperature (40, 55, 70 °C and different co-solvent percentage (2.5, 5, and 7.5 % ($V_{ethanol}/V_{solvent}$)). The extraction time was 3 hours respectively. The optimum condition were 29.95 MPa, 40 °C and 6.49 % ($V_{ethanol}/V_{solvent}$) with 14.95 % yield and 8.47E-12 m^2/s diffusivity coefficient.

Keywords: Peanut skin, CO_2 supercritical fluid extraction, yield, diffusivity coefficient

INTRODUCTION

Peanut is an agricultucal product that has been used for ingredient of traditional dishes especially for asian country such as Malaysia, Indonesia, China, India, Vietnam, etc. Up to this date, peanut skin is always been removed from the industry as waste of industrial process. This is because peanut skin contains astrigent taste that may affect on the quality of product, for example, peanut butter and peanut oil. Although peanut skin is an industrial product waste, it is rich in antioxidant such as procyianidin, catechin, epicatechin and anthocyianidin [1-4] that may contribute much benefit on economic and human health. Most of these antioxidant activities have been associated with reduced risk of cardiovascular diseases, anti diabetic, anti inflammantory, and cancers [3].

Supercritical carbon dioxide extraction (SC-CO_2) is a green technology to extract oil, antioxidant, and bioactive compounds. Carbon dioxide does not leave residues after the completion of extraction process. Supercritical carbon dioxide extraction has been done by many researchers to extract bioactive compund from plants and herbs effectively. Recent years, supercritical fluid extraction has been reported to successfully extract many kinds of herbs and plants such as *Pithecellobium Jiringan* (Jack) Prain seeds, palm oil, pipper batle leaves, and rubber seeds oil [5-9].

The supercritical carbon dioxide extraction has many advantages: the extract has high purity on solute content, the extract are free of organic solvent, easy to separate extract and solvent, supercritical fluid extraction has high selectivity to certain compound in the solute, and it is a nontoxic solvent. Commonly, supercritical fluid extraction in food process uses carbon dioxide because CO_2 is easily found, not expensive as solvent, and also has small critical temperature and pressure (31.1 °C and 7.1 MPa). The key factor of supercritical carbon dioxide was the solubility of solvent which can be manipulated by pressure and temperature [10].

The presence of ethanol bipolar compound is needed for this extraction process to encourage the extraction due to its polarity that can increase the polarity of CO_2 supercritical extract polar bioactive compound. Moreover, ethanol is safer than other commonly used modifier such as methanol, propanol, and butanol.

The extraction from natural materials such as plant, seed or nut may involve diffusion and mass transfer process due to the occurrence of releasing solutes from porous or cellular solid matrices into solvent. Mass transfer as the net mass movement from one location (solute) to solvent during the extraction process [11] depends on the differences in chemical potential. It is mainly used to explain the physical processes of chemical species involving diffusive and convective transport. Mass transfer thermodynamically described in terms of rate function, which depends on substance diffusivities and flow pattern within the system. Based on the diffusivity coefficient, the process behaviour can be evaluated and determined which is the main influences operation conditions to maximize the yield extract and diffusivity of solvents.

Response surface methodology (RSM) has been successfully used to determine the influence of variables on the supercritical carbon dioxide extraction. Commonly, in the supercritical carbon dioxide extraction, pressure, temperature, flow rate of carbon dioxide, and co-solvent percentage are the variables of extraction process. Up to this date, RSM has been successfully used to determine the optimum condition to obtain bioactive compound and yield extract for example extraction of red-fleshed pitaya [12], piper battle linn leaveas [13], tomato skin [14], Passiflora seed oil [15], and palm oil [16].

The purpose of this work is to determine the best conditions of extraction for extraction yield and diffusivity coefiicient using CO_2 supercritical carbon dioxide extraction and co-solvent ethanol.

EXPERIMENTAL

Chemical

Liquid carbon dioxide (99% purity) was used in the supercritical extraction apparatus purchased from Kras Instrument, Johor Bahru, Malaysia. Technical grade of ethanol (99.86%) was obtained from Permula Sdn. Bhd., Johor Bahru Malaysia.

Plant material

Peanut skin was obtain from G-Tachfood Industries Sdn. Bhd. Peanut skin was dried in oven at 60 °C for 4 hours. Dry peanut skin obtained was blended into powder, classified to size of particle 425 µm with shaving process, stored in a plastic sample, and placed in the freezer until used (−20 °C).

Experimental procedure

A set of laboratory scale supercritical carbon dioxide extraction was used for this experiment. Extraction process was performed at temperature of 40, 55, and 70 °C, with a pressure of 10, 20, and 30 MPa, percentage of co-solvent 2.5, 5, and 7.5 % ($V_{ethanol}/V_{total}$), and CO_2 flow rate of 3 mL/minute. The extraction time was 180 minutes. Chiller temperature was set at 6 °C while the heater on the back pressure regulator (Jasco BP 2080 Plus Automated BPR) was set at 50 °C. Next, 5 ±0.005 g of peanut skin was placed into extraction vessel. Then, liquid CO_2 was pumped by HPLC pump (Lab Alliance, Series II Pump) from the CO_2 tank into the system continuously with a supercritical pump at a flow rate of 3 mL/min, and also ethanol as co-solvent 98.86% was pumped continuously when the desired temperature was achieved. The extracted oil was collected by vial and it was recorded for every 30 minutes of the extraction process.

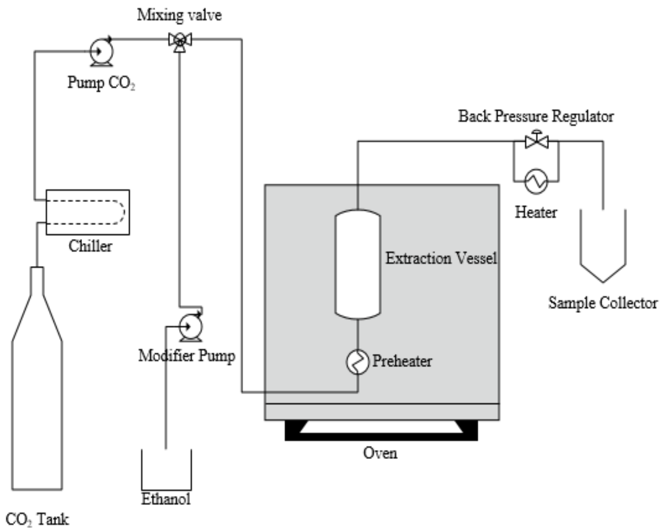

Fig. 1 Schematic diagrams of supercritical fluid extraction apparatus.

Analysis of extract yield

The extract yield was calculated using the following Eq. (1),

$$\text{Extract Yield (\%)} = \frac{m_a}{m_{ab}} \times 100\ \% \quad (1)$$

where m_a is mass of the extract in gram and m_{ab} is mass of sample in gram.

Diffusivity by Single Sphere Model

Diffusion is assumed to occur in a sphere surface particle solute. Diffusion of supercritical CO_2 and ethanol as co-solvent in sphere equations is used to determine the diffusivity of solvent to solute [17]. The diffusion equation for a constant diffusion coefficient takes the form of Eq. (2).

$$Y' = \frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\exp\frac{D_e t n^2 \pi^2}{R^2} \quad (2)$$

where *Mt* is the total amount of diffusing substance which has entered the sheet at specific time, *M∞* is the corresponding quantity after infinite time, D_e is diffusivity, R is radius of particle solute, and *t* is time.

The assumptions of single sphere model are intra particle of mass transfer is the main factor in the extraction process, resistance of mass transfer is zero, solute in a column extraction is porous inert sphere, all of particle size is similar, all of solute in the bed is extracted, and component to be extracted move through the particles by a process 'similar to diffusion' [18].

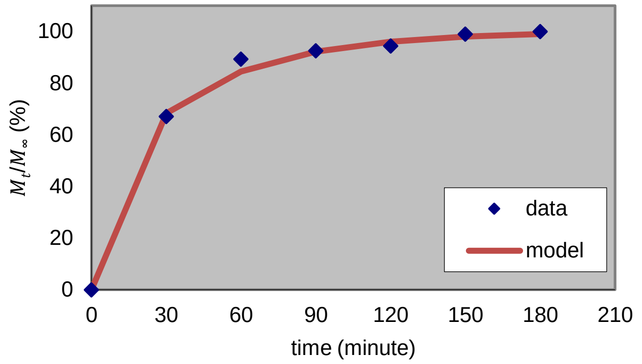

Fig. 2 Extraction kinetics of peanut skin oil: comparison of experimental data and single sphere model at pressure 30 MPa, temperature 40 °C, and percentage of co-solvent 5%.

Fig. 2 shows that single sphere model correlate the experimental data at 30 MPa, 40 °C and 5 % percentage of co-solvent. The single sphere has been successfully correlate the experimental data with minimum error. The general equation of single sphere model (SSM) is applicable for high velocity and high pressure but fail to represent the extraction behavior at low velocity and pressure due to %AARD between model and experimental data [19]. The solver of Microsoft Excel 2013 was used to calculate of diffusivity coefficient in this study.

Experimental design

An experimental design was performed to optimize three important parameters of SC-CO_2 extraction which are pressure (X_1), temperature (X_2), and co-solvent percentage (X_3) to achieve the optimum yields of peanut skin extracts and diffusivity coefficient. Box Behnken Design was applied for experimental design.

Table 1 Factors and levels tested for the experimental design.

Factors	Low Level	Medium Level	High Level
Pressure,(X_1, MPa)	-1	0	+1
Temperature,(X_2, °C)	-1	0	+1
Percentage of co-solvent (X_3, %)	-1	0	+1

RSM was applied to optimize the operating parameters of SC-CO_2 for the extraction of peanut skin. RSM model or regression equation which include linear and quadratic variables as well as interaction terms were used to fit the first and second-order polynomial equation based on the experimental data as follows:

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_i X_i^2 + \sum_i \sum_j B_{ij} X_i X_j \quad (3)$$

where Y is the predicted response, B_0 is a constant, B_i, B_{ii}, B_{ij} are the interaction of effect, X_i and X_j are coded value of factor. Finally, the response surfaces of the variables inside the experimental domain were analyzed by analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Experimental results

The effect of temperature, pressure, and percentage of co-solvent ethanol on extract yield with SC-CO_2 was investigated using the second order polynomial and linear with interaction statistical model. The levels of independent variables used in this experiment were determined based on preliminary experiments. The linearity and quadratic effect of the treatments variables, their interactions and coefficients on the response variables were obtained by analysis of variance (ANOVA) the two-level face-centered design was used to determine the interaction effects of the operating condition such as pressure, temperature, and percentage of co-solvent ethanol with response yield extract and diffusivity coeffiecient. Experimental design was made by using box bhenken design shown in Table 2.

Table 2 The experimental design for the SC-CO_2.

Run	Pressure, MPa X_1	Temperature, °C X_2	Percentage of Co-solvent,% X_3	Yield extract,%	Diffusivity Coefficient, m^2/s
1	+1	0	+1	14.60	8.98E-12
2	-1	0	+1	11.53	2.98E-12
3	0	0	0	14.17	5.34E-12
4	+1	0	-1	9.91	7.88E-12
5	0	+1	-1	10.06	3.08E-12
6	-1	+1	0	12.14	4.24E-12
7	0	-1	-1	12.12	3.98E-12
8	0	0	0	14.17	4.73E-12
9	0	-1	+1	15.27	5.98E-12
10	0	0	0	14.18	4.73E-12
11	0	+1	+1	14.86	6.25E-12
12	+1	-1	0	13.96	6.48E-12
13	-1	-1	0	12.35	2.18E-12
14	-1	0	-1	7.41	1.41E-13
15	+1	+1	0	15.40	3.88E-12

The highest amount of yield extract as experimental data was 15.27 % with pressure 20 MPa, temperature 40 °C and 7.5% percentage of co-solvent. The lowest yield of the extract was 7.41% with pressure 10 MPa, temperature 55 °C and 2.5% percentage of co-solvent ethanol. The highest diffusivity diffusivity coefficient was obtain at pressure 30 MPa, temperature 55 °C and 7.5% percentage of co-solvent ethanol was 8.90E-12 m^2/s. the lowest diffusivity coefficient was 1.14E-13 at pressure 10 MPa, temperature 55 °C, and 2.5% percentage of co-solvent ethanol.

Statistical data analysis

The statistical analysis of experimental data, second order polynomial equation has succesfully optimized the extract yield of peanut skin and first order polynomial was suitable to optimize diffusivity coefficient data. The analysis of variance (ANOVA) is presented in Table 3. The analysis showed that both models were statistically significant (sig. < 0.05) at 95% confidence. The calculated coefficients of all factors are shown in Table 3 and 4.

Effect of operational condition on the extract yield

In this study, effect of pressure, temperature, and percentage of co-solvent were used for determination of influence for supercritical CO_2 extraction and co-solvent ethanol. Table 2 shows the response of extract yield and diffusivity coefficient of peanut skin. The coefficient of regression model for extract yield was second order polynomial as shown in Table 3 and can be written as Eq. 4:

$$Y = (14.18 + 1.30X_1 - 0.16X_2 + 2.09X_3 - 1.46X_1^2 + 0.75X_2^2 - 1.85x_3^2 + 0.41X_1X_2 + 0.14X_1X_3 + 0.41X_2X_3) \quad (4)$$

The second order polynomial model has been succesfully described the response surface of extract yield due to satisfactory coefficient determination (R^2) 0.97 as shown in the Fig. 5 and p-value 0.0017. From Table 4, the extract yield on second order polynomial indicated that linear percentage of co-solvent ethanol, quadratic percentage of co-solvent ethanol, quadratic pressure, and pressure were highly influence in this extraction process because based on the equation model, had bigger values of coefficient compared with others. Therefore, these results suggest that linear effects, cubic and second polynomial model of the independent variables may be the primary determining factors affecting the extract peanut skin yield.

Table 3 Anova table for response.

Source	Sum of square	df	Mean Square	F	p-value
Extract Yield					
Regression	73.09	9	8.12	21.56	0.0017
Residual	1.88	5	0.38		
Total	74.97	14			
Diffusivity coefficient					
Regression	5.61E-23	6	9.36E-24	5.34	0.017
Residual	1.40E-23	8	1.75E-24		
Total	7.02E-23	14			

Table 4 Coefficient of polynomial functions of extract yield.

Extract yield (%)	Coefficient (β)	Standard Error	p-value
B_0	14.18	0.35	0.17 E-2
X_1	1.30	0.22	0.18 E-2
X_2	-0.16	0.22	0.50
X_3	2.09	0.22	0.0002
X_1^2	-1.46	0.32	0.0060
X_2^2	0.75	0.32	0.06
X_3^2	-1.85	0.32	0.0022
X_1X_2	0.41	0.31	0.23
X_1X_3	0.14	0.31	0.66
X_2X_3	0.41	0.31	0.23

R^2 = 0.97

Table 5 Coefficient of polynomial functions of diffusivity coefficient.

Diffusivity Coefficient (m^2/s)	Coefficient (β)	Standard Error	p-value
B_0	+4.72E-012	3.42E-13	1.69E-2
X_1	+2.21E-012	4.68E-13	1.5E-3
X_2	-1.46E-013	4.68E-13	0.76
X_3	+1.13E-012	4.68E-13	0.04
X_1X_2	-1.16E-012	6.62E-13	0.17
X_1X_3	-4.34E-013	6.62E-13	0.52
X_2X_3	+2.92E-013	6.62E-13	0.67

R^2 = 0.80

From Fig. 3, 3D response shows that the extract yield increase with increasing of pressure X_1 at constant lowest and highest temperature X_2. Increasing of pressure will affect the density of CO_2. Therefore, increasing of density will increase the solvent power on the extraction process. Moreover, increasing of solvent power will enhance the solubility of extract to solvent that easily extract went out from the solute [20]. This is simillar funding with extraction of castor oil (*Ricinus comminis L.*) that increasing of pressure will increase the yield of oil. This is due to density of solvent that increases the pressure will increase the density of supercritical carbon dioxide. Therefore, the extract is easily extracted from solute [21].

Increasing of the temperature at low pressure and high pressure slightly enhanced the yield extract of peanut skin. It is proofed that in the Table 4, p-value of pressure X_1 is lower than p-value (0.05 > 0.0017). This is because the effect of vapor pressure on the supercritical CO_2 that carbon dioxide easily diffuse to solute and carry away the extract [9]. However, the influence of temperature is not dominant for this experiment to obtain extract yield due to significant number. P-value temperature is higher than p-value (0.5034 > 0.05). This is simillar funding with extraction of spilanthol from *Spilanthes acmella* flowers that increasing of temperature increased the yield extract. This is because the effect of vapor solute increase the spilantthol extract from solute [22].

From the Fig. 4, the percentage of co-solvent is the main influence variable for extraction of peanut skin by supercritical fluid extraction. Ethanol as co-solvent or modifier, is a polar compound that can easily extract the polar compound from the solute [3]. The percentage of co-solvent had a smaller value of significant than pressure (0.0002 < 0.0017). This is because the compositions of peanut skin extracts are polar compounds such as catechin, epicatechin, procyanidin and anthocyanidin that increasing of percentage of co-solvent will enhance the polarity of supercritical CO_2 that the percentage of extract will increase [3]. Furthermore, ethanol as co-solvent opens the porosity of peanut skin that extract is easily carried away by solvent [23]. The additional ethanol in SC-CO_2 caused the swelling of the matrix, thus increasing the internal volume and the surface area contacting between solute and solvents [23].

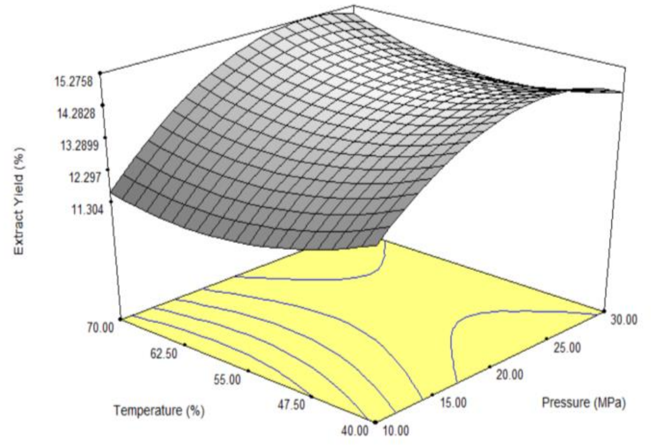

Fig. 3 3D response for the effect of temperature and pressure on the extract yield.

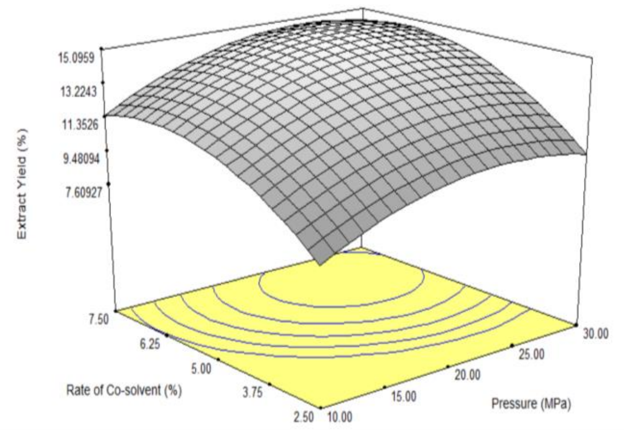

Fig. 4 3D response for the effect of temperature and pressure on the extract yield.

The optimization result of the extraction of peanut skin by supercritical fluid extraction with co-solvent ethanol was at pressure 30 MPa, temperature 40 °C and 6.49% percentage of co-solvent ethanol obtained 14.05% extract yield. The calculated coefficient of correlation (R^2) of the optimization of extraction with response yield extract was high confident (0.97 > 0.950) can be seen in Fig. 5 that model successfully follow the actual value of yield extract. However, the experimental results obtained from the approximate model did not suggest the optimal conditions on pressure X_1 and temperature X_2 in which the highest extract yield was obtained.

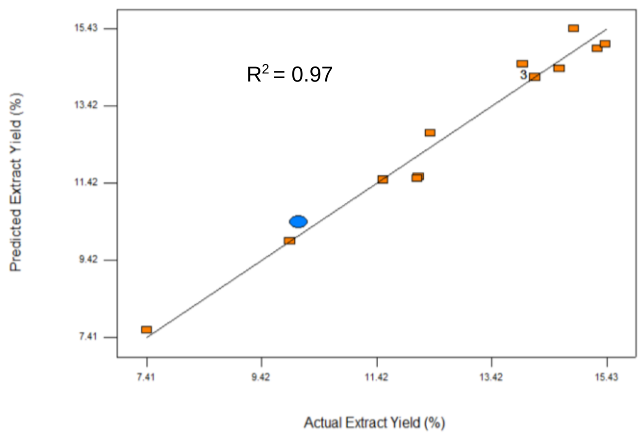

Fig. 5 Predicted values vs actual values for extract yield of peanut skin

Effect of operational condition on the diffusivity coefficient

In this study, effect of pressure, temperature, and percentage of co-solvent on diffusivity coefficient were investigated to obtain a optimum diffusivity coefficient. Table 2 and 5 show the response of diffusivity coefficient and interaction of parameters. The coefficient of regression model for diffusivity coefficient was first order polynomial with interaction as shown in Table 3 and can be written on Eq. 5:

$$Y = (4.724 + 2.210X_1 - 1.461X_2 + 0.1139X_3 - 1.165X_1X_2 - 0.4349X_1X_3 + 0.2923X_2X_3) * 10^{-12} \quad (5)$$

First order polynomial model has been succesfully described the response surface of diffusivity coefficient due to satifactory coefficient (R^2) of response was high (0.80) as shown in the Fig. 8 and p-value (0.0017). From Table 5, for the diffusivity coefficient on the linear with interaction model indicated that linear pressure, temperature, and interaction between pressure and temperature were highly influence because it had big values of coefficient compared with others. Therefore, these results suggest that linear effects of the independent variables may be the primary determining factors affecting the diffusivity coefficient.

From Table 5, Pressure X_1 was significant, it proved that in the Table 5 p-value of pressure X_1 is lower than p-value (0.05 > 0.015) and also the effect of pressure is the most influence because of coefficient of pressure is the highest in the linear with interaction model.

From Fig. 6, increasing of percentage of co-solvent ethanol at the lowest pressure and the highest pressure slightly increase the diffusivity coefficient of extraction peanut skin process. However, the percentage of co-solvent is the main influence variable for extraction of peanut skin by supercritical carbon dioxide extraction. Ethanol as co-solvent or modifier encourage carbon dioxide to carried out the extract from solute of peanut skin due to polarity of solvent. Ethanol increase the polarity and solubility of solvent that easily diffuse to solute. Furthermore, Ethanol as co-solvent opens the porosity of peanut skin that extract is easily carried away by solvent. It is similar with the finding of Astaxanthin extraction from *Haematococcus pluvialis* that ethanol as entrainer enhance the solubility and diffusivity of solvent to solute and ethanol as modifier opens the porosity of *Haematococcus pluvialis*. Therefore, astaxanthin is easily carried away by solvent [23].

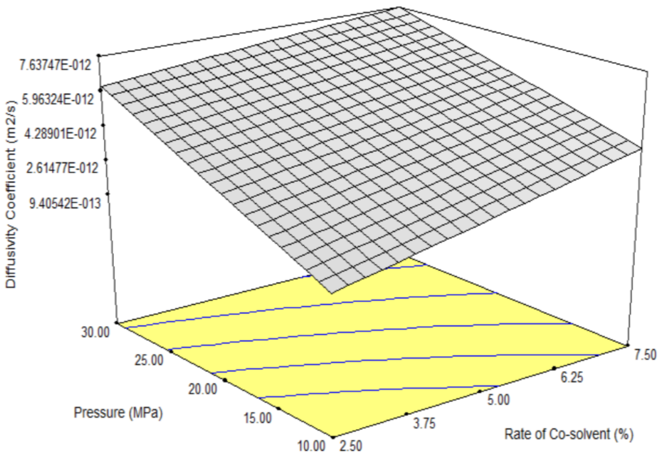

Fig. 6 3D response for the effect of percentage of co-solvent and pressure on the diffusivity coefficient.

From Fig. 7, 3D response shows that increasing pressure X_1 at lowest and highest temperature X_2 increase the diffusivity coefficient. This is because increasing of pressure will increase the density of carbon dioxide as solvent. Increasing of density will increase the particle carbon dioxide inside of solvent. Therefore, much particle carbon dioxide in the solvent easily make a bond with compound in the solute of peanut skin. It is simillar condition with extraction of is Pithecellobium Jiringan (Jack) Prain Seeds by Yunus et al. (2012).

Although, increasing of the temperature at lowest pressure enhance the diffusivity coefficient extraction of peanut skin, at highest pressure, increasing of temperature decrease the diffusivity coefficient of extraction process. This is because the effect of solute vapour pressure is dominant in the lowest pressure than in the highest pressure. In the lowest pressure, the effect of solubility was dominant in that process because increasing of temperature X_2 will decrease the solubilty of solvent. Effect of temperature X_2 is significant in this experiment because p-value of temperature is lower than p-value (0.041 < 0.05). Temperature, X_2, as variable of process was influence to the experiment due to coefficient on the linear with interaction.

The optimization result of the extraction of peanut skin by supercritical fluid extraction with co-solvent ethanol was at pressure 30MPa, temperature 40 °C and 6.49% percentage of co-solvent ethanol obtained 8.48×10^{-12} m^2/ s diffusivity coefficient. The calculated coefficient of correlation (R^2) of the optimization of extraction with response yield extract was high (0.80) can be seen in Fig. 8 that model successfully follow the actual value of yield extract. Nevertheless, the experimental results obtained from the approximate model did not suggest the optimal conditions on pressure X_1 and temperature X_2 in which the highest diffusivity coefficient was achieved.

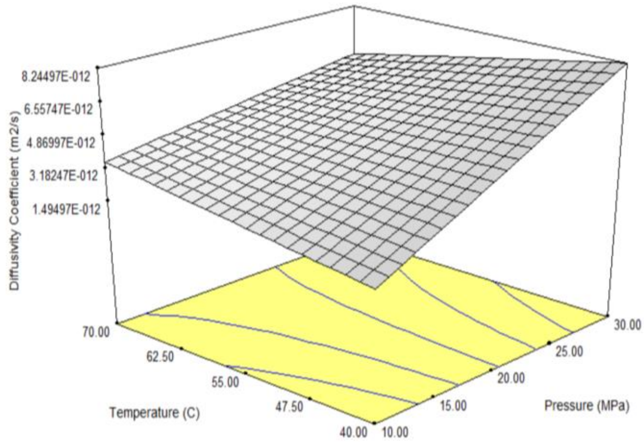

Fig. 7 3D response for the effect of temperature and pressure on the diffusivity coefficient.

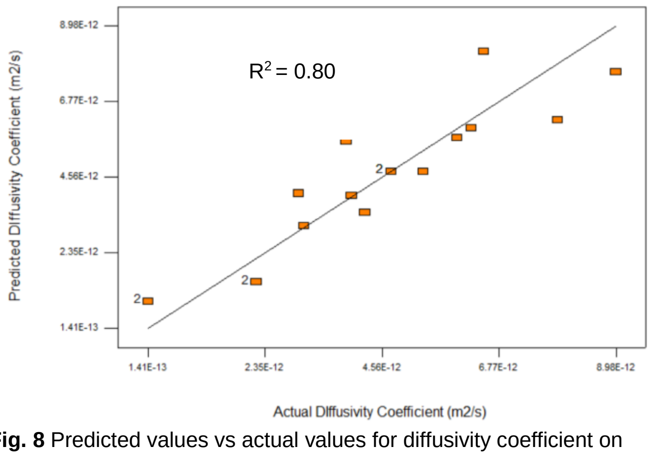

Fig. 8 Predicted values vs actual values for diffusivity coefficient on extraction.

CONCLUSION

The second order polynomial model was adequate in optimizing the supercritical carbon dioxide extraction with co-solvent ethanol of yield extract peanut skin, but failed to adequate for diffusivity coefficient. Determination of diffusivity coefficient is important to determine the mass transfer of solvent and solute. First order polynomial with interaction was succcesfully capable to optimize diffusivity coefficient on the carbon dioxide supercritical fluid extraction. The independent variables using second order polynomial and first order polynomial with interaction model significantly ($p < 0.05$) influenced the extraction yield extract and diffusivity coefficient. On the second order polynomial model and first order polynomial with interaction, a synergetic effect of temperature had no significant effect ($p > 0.05$). The highest estimated recovery of peanut skin extract yield and diffusivity coefficient with SC-CO_2 extraction and co-solvent ethanol was about 14.94% and 8.49×10^{-12} m^2/s. The model predicts the highest peanut skins extract yield at 40 °C, 30 MPa and 6.49% percentage of co-solvent. Based on the estimation data, at lower temperature and high pressure will give the maximum yield peanut skins extract and diffusivity coefficient and prevent the extract from degradation bioactive compound inside the extract. At higher percentage of co-solvent ethanol will maximize the extraction process to carried away bioactive compound such as catechin from the solute particle due to enhancement of polarity of solvent [4]. From the optimization of diffusivity data, optimum variables obtained can be used as references to obtain maximum mass transfer process between peanut skin as solute and carbon dioxide as solvent with ethanol as co-solvents.

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