Extraction and Solubility Modeling of Anthocyanins Rich Extract from *Hibiscus sabdariffa* L. using Supercritical Carbon Dioxide

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Abstract

This study aimed to evaluate the extraction yield, and anthocyanins content of *Hibiscus sabdariffa* L. calyces extract using different temperatures (T) at 50 - 70°C, pressure (P) at 8 - 12 MPa, and modifier ratio at 5 - 10%. This work used a supercritical carbon dioxide (SC\textsubscript{2}CO\textsubscript{2}) extraction with ethanol and water as a modifier. The solubility of the extract was then measured before correlating using Chrastil, del Valle & Aguilera (dVA), and Adachi-Lu (A-L) models. This study revealed that a low T and increase in P at a constant modifier ratio would boost the anthocyanins content, contradicted with the extraction of total yield value, which is higher when increase T and low P. Meanwhile, analyzed results show that the solubility of *Hibiscus sabdariffa* calyces' extracts has successfully fitted the Chrastil's model with AARD of 27.72% as compared with dVA (35.42%) and A-L models (50.23%).

Keywords: *Hibiscus sabdariffa*, Anthocyanins, Supercritical carbon dioxide, solubility, modeling.

Introduction

*Hibiscus sabdariffa* L. (*H. sabdariffa*) or Roselle is a tropical annual herb plant that belongs to Malvaceae family\textsuperscript{1}. The calyces are rich in anthocyanins, the red color pigment. It is abundantly found in Malaysia and has become one of the most important commercial crops. The fleshy red calyces' components in *H. sabdariffa* are the most frequently used to make wine, syrup, or ice cream. Meanwhile, the dry calyces are limitedly used for tea and infusion drinks\textsuperscript{2}. The major components found in *H. sabdariffa* anthocyanins are delphinidin-3-sambubioside, cyanidin-3-sambubioside, and cyanidin-3-glucoside\textsuperscript{3}. Anthocyanins are flavonoid pigments soluble in water and have been extensively used in food ingredients such as industrial colorants, supplements, and health-promoting food. Due to its anti-inflammatory, antioxidant, and anti-carcinogenic properties, anthocyanins as food colorants could improve the overall appearance and have beneficial health effects on several chronic diseases\textsuperscript{3-5}. These positive effects of anthocyanins have initiated extensive research on their benefits, applications, and extraction techniques. It is acknowledged that acidified solvent extraction is the most common method of extracting anthocyanins using polar solvents like water, ethanol, and methanol\textsuperscript{6-8}. Pragalyaashree et al.\textsuperscript{6} discovered that acidified ethanol with acid hydrochloric gave the highest anthocyanin extract of 3.35 mg/g dry *H. sabdariffa* calyces. Due to the requirements in industries (e.g., environmental, public health, and energy factors), the use of...
greener extraction methods in the food and chemical sectors has gained considerable attention. Supercritical carbon dioxide (SC-CO₂) extraction with polar solvent as modifier has been introduced for anthocyanins extraction in several plants such as purple corn cob, Crocus sativus petals, chokeberry, haskap berry pulp, jucara, and H. sabdariffa. Small amounts of polar modifiers, like water and ethanol, were added to enhance SC-CO₂ solvent strength, an affinity for poorly soluble solutes, and, eventually, extraction yield. The presence of water could produce in situ carbonic acids and provide low pH conditions to increase cell membrane permeability, resulting in cell disruption and could release the anthocyanins from calyx's vacuole. It has been shown that SC-CO₂ extraction methods seem to have a high recovery yield for bioactive compounds compared to conventional methods by manipulation of SC-CO₂ conditions. Other than that, SC-CO₂ can be more advantageous than other advanced extraction methods in terms of purity, antioxidant activity, antibacterial activity, and thermal stability of the extracts obtained.

Pimentel-Moral et al. applied SC-CO₂ extraction with ethanol as a modifier to recover phenolic and organic acids in H. sabdariffa calyces. Our previous study optimized the SC-CO₂ conditions on H. sabdariffa calyces extract yield within the experimental range of parameters in this work. However, this work was further performed to compare and evaluate the effect of temperature, pressure, and cosolvent ratios between total extraction yield and anthocyanins compound.

Solubility refers to the maximum amount of extracted solute at a saturation equilibrium. Solubility measurement can be conducted by experimental or modeling. Semi-empirical models were chosen to determine the solubility behavior, thus supporting the design and identification of SC-CO₂ operating conditions. Chrastil developed the most common semi-empirical models to analyze the solubility of the solution. At the same time, Adachi-Lu (A-L) and del Valle and Aguiler (dVA) were modified with a few parameters into the initial equations. As far as we know, only Lukmanto et al. has been focusing on the solubility data of H. sabdariffa, specifically only on phenolic compounds using the extraction of SC-CO₂ with acetone modifier.

Therefore, the purposes of this study were to assess the effect of the SC-CO₂ extraction temperature, pressure, and modifier ratio on total extraction yield and cyanidin 3-glucoside as one of the anthocyanins compounds in H. sabdariffa calyces and to correlate the extraction solubility data with three different semi-empirical models by Chrastil, A-L, and dVA, respectively. Three different conditions: temperature (50 - 70 °C), pressure (8 - 12 MPa), and modifier ratio (5% - 10%) of 6 mL/min of solvent flow rate were used in this study implementing SC-CO₂ extraction technique.

Materials and methods

Materials

Dry H. sabdariffa calyces from the UMKL variety were purchased from Ekomekar Resources, Terengganu, Malaysia. The dried calyces were ground and mesh sieved to achieve a range of sizes of 200 - 355 μm. A screw-capped glass bottle was used to keep the sample, protect it from light, and placed at −18 °C for further use.

Chemicals

Carbon dioxide (99.9%) was purchased from KRAS Instrument Sdn Bhd (Malaysia), while the absolute ethanol (99.89%) and acetonitrile were bought from Sigma-Aldrich (Singapore). On the other hand, kuromanin chloride (cyandin 3-glucoside) was obtained from Extrasynthese (German).

SC-CO₂ extraction

As shown in Figure 1, H. sabdariffa calyces were extracted using a lab-scale of SC-CO₂ extractor, assisted by ethanol: water (75:25 v/v) as a modifier. Samples were taken out of the freezer and stored at room temperature for thawing purposes. 1500 mg of dry H. sabdariffa powder was placed into an extraction vessel before being tightly sealed. The chiller temperature was set at 6 °C, while the heater on the backpressure regulator (Jasco BP 2080 Plus Automated BPR) was set at 50 °C. Next, liquid CO₂ was pumped by a CO₂ pump (Lab Alliance, Series II) equipped with an automated flow rate meter.
Modifier was also pumped using a 10 mL Series II pump (Scientific Systems, Inc., USA) with three modifier ratios of 5, 7.5, and 10% from a total solvent flow rate of 6 mL/min as determined in our preliminary study. The desired temperature of 50, 60, 70 °C and pressure of 8, 10, 12 MPa were set. Because of the cost-effective approach to developing high-quality plant extracts, a low-pressure CO$_2$ was chosen. The pressure was controlled by an automated back pressure regulator (Jasco BP 2080 Plus Automated BPR, Japan). The extraction of SC-CO$_2$ was started after achieving the required temperature and pressure. Within 80 min of the total extraction time, the extraction process was dynamically performed. Subsequently, the extract was placed in a centrifugal vacuum concentrator (Mivac Duo, UK) at 40 °C to evaporate the solvent. The extract was then placed in a freezer at -20 °C for further investigation. The extract yield of *H. sabdariffa* was determined as given in Equation 1.

\[
\text{Total yield } [\text{mg/g}] = \frac{\text{Mext (mg)}}{\text{F (g)}}
\]

where Mext is the total extracted mass and F is a feed mass on a dry basis.

**Figure 1.** Schematic diagram of the SC-CO$_2$ experimental setup.

**Determination of anthocyanins content**

The quantification of monomeric anthocyanins (cyanidin 3-glucoside) was performed using Waters Breeze 2 High-Performance Liquid Chromatography (HPLC) equipped with 2475 multi λ fluorescence detector, 717 plus autosampler, 1525 Binary HPLC pump, and temperature control module. For cyanidin 3-glucoside detection at 520 nm, the 460 mm/250 mm/5 mm (MERCK, Darmstadt, Germany) RP C18 column was used with excitation and emission wavelength. Acetonitrile: water at a ratio of 65:35 was used as a mobile phase solvent and pumped at 1.0 mL/min. 30 °C of column temperature was fixed with a sample volume of 20 μL for injection. The compound was identified based on their retention time by comparing the sample's chromatography peak to the standard. The value of anthocyanin content was expressed in the mg cyanidin 3-glucoside/g sample.

**Semi-empirical modeling**

**Calculation of solubility of total yield extract in SC-CO$_2$**

Based on the calculation in Equation 2, the solubility (S) of the extract is the difference between the mass of extracted yield (g) and the variation of volume of carbon dioxide (L) used. The low percentage used for modifier was ignored in the solubility calculation in this section due to only minor changes in density at constant temperature and pressure.
\[ S = \frac{\Delta y}{\Delta x[L]} = \frac{y_a - y_x}{x_a - x_x} \quad (2) \]

**Chrastil Model**

Based on the Chrastil model, temperature is the crucial parameter that affects the solubility of the solute. It was determined by taking the equilibrium of the solvent molecules into account. Equation 3 shows the solubility \( S \) equation:

\[ S = \rho_{CO_2}^k \exp\left(\frac{a}{T} + b\right) \quad (3) \]

The Chrastil model describes a relationship between the solute solubility, \( S \) (g/L), and SC-CO\(_2\) density (g/L). The value of \( k \) defines the number of SC-CO\(_2\) in solvated complex, \( a \) is related to the extraction enthalpy (enthalpy of solvation and vaporization), \( b \) depends on the molecular weight of the solute and solvent, and \( T \) is temperature conditions (K).

**Del Valle Aguilera (dVA) Model**

Del Valle Aguilera further developed Chrastil's model. The addition of one adjustable parameter is related to temperature, thus maximizing the temperature dependency instead of density. The dVa equation is expressed as follows:

\[ S = \rho_{CO_2}^k \exp\left(\frac{a}{T} + \frac{b}{T^2} + c\right) \quad (4) \]

The adjustable parameters are the value of \( a \) and \( b \), which correlates to the thermal effect. Meanwhile, the value of \( c \) depends on the molecular weight of the solute and the solvent, and \( T \) is temperature conditions (K).

**Adachi-Lu (A-L) Model**

Adachi-Lu Model (A-L) is another variety of Chrastil models. This model assumed that the density of solvent has a significant impact on the solubility of extract. The association number (or coefficient), \( k \), is thus modified to a quadratic polynomial. The A-L equation is shown in Equation 5.

\[ S = [k_1 + c\rho_{CO_2} + d\rho_{CO_2}^2]\ln\rho_{CO_2} + \frac{a}{T} + b \quad (5) \]

Coefficient values of \( k_1 \), \( c \), and \( d \) are the adjustable parameters to obtain the overall equilibrium constant and represent the average number of solvent molecules. \( a \) is the adjustable parameter, which correlates to the thermal effect, while the value of \( c \) depends on the molecular weight of the solute and the solvent. \( T \) remains as a temperature condition (K).

**Statistical analysis**

For statistical analysis, the average absolute relative deviation percentage (AARD\%) was used in this study as it provides information on the error of agreement between the model and the experimental data. The equation for AARD\% is shown in Equation 6 below:

\[ \text{AARD\%} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\ln S_{\text{model}} - \ln S_{\text{exp}}}{\ln S_{\text{exp}}} \right| \quad (6) \]

where \( n \) is the number of data points, \( S_{\text{exp}} \) is the experimental solubility data (g/L), and \( S \) model is the solubility of model data (g/L).

**Results and discussion**

**SC-CO\(_2\) experimental results**

Table 1 shows the experimental conditions used in this study and their effects on total yields, anthocyanins content, and extraction solubility of \( H. \) sabdariffa. The total yield ranged from 59.29 mg/g
and 279.60 mg/g. Meanwhile, the anthocyanin concentration range was relatively narrow, ranging from 10.12 to 12.41 mg/g. H. sabdariffa extract solubility was calculated to be between 0.41 and 3.29 g extract/L CO₂.

Table 1. Experiment results (yield and anthocyanins) and solubility data were obtained from SC-CO₂ operating conditions.

| Pressure, MPa | Temperature, °C | Modifier Ratio [%] | Total Yield [mg/g] | Anthocyanins Content [Cya-3-glu, mg/g] | Solubility [gextract/LCO₂] |
|--------------|----------------|-------------------|--------------------|--------------------------------------|---------------------------|
| 8            | 50             | 5                 | 88.73              | 10.28                                | 0.52                      |
|              | 5              | 179.03            | 10.96              | 0.82                                 |                           |
|              | 10             | 177.47            | 10.55              | 0.83                                 |                           |
| 8            | 60             | 5                 | 119.95             | 12.41                                | 0.89                      |
|              | 7.5            | 240.90            | 10.58              | 2.02                                 |                           |
|              | 10             | 175.71            | 10.12              | 3.29                                 |                           |
| 8            | 70             | 5                 | 168.01             | 11.94                                | 0.69                      |
|              | 7.5            | 268.83            | 10.28              | 3.23                                 |                           |
|              | 10             | 225.50            | 10.15              | 0.91                                 |                           |
| 10           | 50             | 5                 | 123.06             | 10.49                                | 0.59                      |
|              | 7.5            | 171.13            | 11.19              | 1.29                                 |                           |
|              | 10             | 174.57            | 10.29              | 0.72                                 |                           |
| 10           | 60             | 5                 | 104.09             | 10.14                                | 0.55                      |
|              | 7.5            | 165.02            | 10.74              | 0.79                                 |                           |
|              | 10             | 215.28            | 10.71              | 1.45                                 |                           |
| 10           | 70             | 5                 | 144.53             | 10.41                                | 1.12                      |
|              | 7.5            | 243.85            | 10.62              | 0.99                                 |                           |
|              | 10             | 279.60            | 10.84              | 1.13                                 |                           |
| 12           | 50             | 5                 | 59.29              | 10.49                                | 0.41                      |
|              | 7.5            | 94.57             | 11.26              | 0.65                                 |                           |
|              | 10             | 103.44            | 11.70              | 0.52                                 |                           |
| 12           | 60             | 5                 | 85.58              | 10.15                                | 0.67                      |
|              | 7.5            | 120.42            | 11.14              | 0.80                                 |                           |
|              | 10             | 139.71            | 10.89              | 1.24                                 |                           |
| 12           | 70             | 5                 | 117.35             | 10.96                                | 0.78                      |
|              | 7.5            | 144.12            | 10.81              | 0.83                                 |                           |
|              | 10             | 214.39            | 12.28              | 1.83                                 |                           |

**Effects of temperature, pressure, and modifier ratio on the extraction yield and anthocyanins content**

Extraction yield is a solvent efficiency indicator for extracting different components from the original material. The yield was calculated by dividing the weight of the extract by the weight of the original sample. Meanwhile, anthocyanin content was calculated by dividing the amount of cyanidin 3-glucoside in the extract by the sample weight. We observed different trends in total yield and anthocyanins content based on pressure, temperature, and modifier ratio. The distinct trend of total yield and anthocyanins demonstrated the selectivity of the SC-CO₂ process.

Figure 3a indicates that the extraction yield increased as the temperature increased from 50 °C to 70 °C at constant pressures of 8 MPa and 12 MPa, respectively. This pattern indicated that as the temperature increased, the total extract became more dependent on the pressure of the solute vapor, resulting in increased diffusivities of both the solvent and the solute. The mobility of CO₂ in the inner matrix was significantly influenced by the decrease in viscosity with increasing temperature. It will easily penetrate and reach the solid matrix's internal interior to recover a large amount of compound. Besides, other compounds in H. sabdariffa extract, such as phenolic acids (gallic acid, caffeic acid, ferulic acids), were more susceptible to temperature. Mohd Nasir reported that increasing the temperature from 50 to 70 °C increased the total extraction yield of Quercus infectoria Galls. This pattern was due to the decrease of
solvent density effect and an increase in solute volatility. Similarly, increasing the temperature reduced viscosity while increasing CO$_2$ penetration into the Piper betel leaves, solute diffusion rate, and extraction yield 50.

On the contrary, the anthocyanins content descended after the operating temperature increased from 50 to 70 °C (Figure 3b). A similar pattern was observed by Maran et al., 31 and Ahmadian-Kouchaksaraie and Niazmard 12, whereby the anthocyanins content started to drop as the temperature rose above 50 °C. At high temperatures, one of the undesirable factors associated with the production of bioactive compounds was the thermal degradation of the solute. Therefore, the finding showed that anthocyanin degradation could have occurred at temperatures higher than 50 °C.

Figure 3. a) Total yield and b) Anthocyanins content (mg cyanidin 3-glucoside/g sample) at various temperatures with a 7.5% modifier ratio.

Meanwhile, when the effects of different pressures on total yield at different temperatures were investigated (Figure 4a), the extraction yield was significantly reduced from 8 to 12 MPa. The decrease in yield with increasing pressure could be attributed to the volatility and polarity of extracted solutes and the interaction of other parameters such as temperature. When the pressure was increased, the deformability of the O=C=O bond of CO$_2$, polarity, density, and solubility of polar solutes increased simultaneously, leading to increased selectivity for specific polar content such as anthocyanins 32, which may have resulted in the other compounds not being extracted.

Figure 4. a) Total yield and b) Anthocyanins content (mg cyanidin 3-glucoside/g sample) at various pressures with 7.5 % of a modifier ratio.

As shown in Figure 4b, the anthocyanin content rose at a constant temperature as the pressure rose from 8 to 12 MPa. The results were similar to those obtained by Ruan et al., 33, who found that increasing the pressure improved the extract's polar compounds (i.e., quercetin and ginkgetin). Mandana et al., 34 discovered similar results using 10 to 30 MPa pressure when extracting bioactive compounds from
spearmint (*Menthas plicata* L.). They observed that increasing the pressure from 10 to 20 MPa increased the extraction yield due to increased SC-CO$_2$ density at higher pressures.

Figures 5a and 5b show the effects of different modifier ratios on the total extraction yield and anthocyanins content at 10 MPa, respectively. Modifiers can improve the polarity of SC-CO$_2$ and facilitate the removal of solute from the plant matrix, thus improving yield and selectivity. By competing with solutes’ active binding sites and altering their matrix structure, polar modifier molecules could speed up the dissociation process $^{35}$. As the modifier percentage increased, the extraction yields increased. High modifier concentrations could also reduce the extract selectivity, depending on the size of phenolic $^{36}$. At 70°C, the same trend was observed with modifier ratios of 5 and 7.5%. When temperatures in the 50 - 60°C range were used, there was no significant increase in yield. Hence, a higher temperature (70°C) with a higher modifier ratio (10%) resulted in significant compound recovery due to improved mass transfer and less selectivity.

Conversely, as shown in Figure 5b, once the condition reached the maximum modifier usage, a larger volume of modifier (10%) was insignificant at a constant temperature of 60 and 70 °C for anthocyanins content. Similar outcomes were observed in SC-CO$_2$ extraction of anthocyanins from Indian blackberry (jamun) $^{31}$ and polyphenols from grape pomace $^{37}$. Results showed that the target bioactive yield was stagnant when the modifier amount increased to a higher value. Manna et al., $^{38}$ reported that this might be due to the modifier fractionation between the supercritical phase and the solid matrix exposed to SC-CO$_2$ could thermodynamically alter the system by ascending the affinity of the solute to the solid phase. It showed that at the end of the process, by adsorbing the ethanol molecules and remaining trapped in the solid matrix, some polyphenols were solubilized.

**Figure 5.** a) Total yield and b) Anthocyanin's content (mg cyanidin 3-glucoside/g sample) in three different modifier ratios (5, 7.5, and 10%) under the constant pressure of 10 MPa.

**A Semi-empirical model for solubility of H. sabdariffa calyces extract**

Temperature and pressure are crucial factors influencing target compound solubility in supercritical fluid extraction, and they are strongly related to the solvating power of fluids in the supercritical phase. In this regard, pressure may influence CO$_2$ density, whereas temperature may impact vapor pressure and diffusivity of target compounds.

The rise in pressure in this study did not improve the solubility due to a small range of pressure parameters (8 to 12 MPa), as shown in Table 1. Nevertheless, when using a wide range of pressure, the high pressure could significantly improve the solute solubility due to an increase in density $^{25}$. Therefore, this finding contradicted the solubility of *Quercus infectoria* galls extracted when using the same extraction technique $^{39}$. They reported that the solubility and solvation power increased when pressure increased to a certain level. Total phenolic and total flavonoid solubility of *Arachis Hypogea* also increased with the enhancement of pressure from 0.00108 to 0.042 mg/Lmix and 0.00056 to 0.00587 mg/Lmix, respectively $^{25}$. Moreover, *Camelia Sativa* seed oil solubility also increased from $6.5 \times 10^{-3}$ to $1.33 \times 10^{-2}$ (kgoil/kgCO$_2$) when operating at a pressure between 35 to 45 MPa $^{40}$. Therefore, to increase
the solubility of the extracted solute, a wide range of pressure will be proposed in further research. Generally, to achieve solute high solubility, a high-temperature condition is preferred. The effect of vapor pressure in the extraction process is very dominant, resulting in higher solubility. Table 1 shows a slight increase in solute solubility as the temperature rose at constant pressure. This result is similar to the peanut skin extract solubility, whereby increasing the temperature enhanced the solubility from $1.28 \times 10^{-3}$ to $7.72 \times 10^{-3}$ \((g_{\text{extract}})/(g_{\text{mix}})\).

### Table 1. Solubility fitting constant for three semi-empirical density-based correlations

| Model    | *P [MPa] | **T [°C] | Modifier ratio | k   | a    | b    | c    | d    | %AARD | ***Av %AARD |
|----------|----------|----------|----------------|-----|------|------|------|------|-------|-------------|
| Chrastil | 8-12     | 50-70    | 5              | 1.24E-6 | 108.15 | 0.37 | -    | -    | 23.57 | 27.72       |
|          |          |          | 7.5             | 0.1 | 78.41 | 0.48 | -    | -    | 23.17 | 35.42       |
|          |          |          | 10              | 1.6E-6 | 159  | 0.77 | -    | -    | 36.43 | 50.22       |
| dVA      | 8-12     | 50-70    | 5              | -0.05 | 329.54 | 0.38 | 0.012 | -    | 24.24 | -           |
|          |          |          | 7.5             | 0.276 | 236  | 0.48 | 0.018 | -    | 48.75 | 50.22       |
|          |          |          | 10              | -0.59 | 1595 | 0.76 | 0.011 | -    | 33.28 | -           |
| A-L      | 8-12     | 50-70    | 5              | -0.018 | -21.48 | 0.81 | 0.003 | -1.35E-4 | 77.50 | -           |
|          |          |          | 7.5             | 0.835 | -7413 | 1.32 | 0.017 | 0.185 | 40.49 | -           |
|          |          |          | 10              | -0.649 | 1382 | 0.75 | 0.001 | -2.4E-6 | 32.68 | -           |

*P= Pressure, **T= Temperature, ***Av % AARD= average percentage of AARD

Semi-empirical models, i.e., Chrastil, dVA, and A-L, were applied to determine the effect of studied parameters on H. sabdariffa calyces extract solubility. The optimum fitting parameters for the correlation were obtained using the least AARD% between model and experimental data. Table 2 shows the fitted parameters used for each relationship. The average AARD (%) of Chrastil, dVA, and A-L models were 27.72%, 35.42%, and 50.22%, respectively. The Chrastil model correlated to the solute solubility with the lowest AARD (%). The lowest percent of AARD showed that the Chrastil was the most successful model and associated with solute solubility compared to other semi-empirical models. Therefore, the coefficient value of the Chrastil model had accurately determined the parameters to enhance the solubility. As described in Equation 3, the coefficient value of \(a\) was related to temperature effects, whether the extraction reaction is exothermic or endothermic. \(a = -\Delta H/R\), where \(\Delta H\) is the sum of the solute’s enthalpy of vaporization and solvation while \(R\) is the gas constant. Besides, the value of coefficient \(b\) depends on the molecular weights of the solute and solvent. The positive value of \(k\) represents an increase in density, which increased \(H. sabdariffa\) calyces extract solubility.

Also, \(k\) refers to the number of solvent molecules that bind with the solute. In contrast, a negative value of \(k\) indicated an increase in solvent density, thus reducing the extract solubility. Therefore, based on the coefficient value obtained, the extraction behavior could be distinguished to enhance the solubility process. In this analysis, a was positive, suggesting that the exothermic reaction was the most acceptable condition to increase the solubility. Due to the negative value of \(\Delta H\), the heat process is unnecessary to enhance the reaction. Therefore, a further increase in temperature will not affect the solvation power of \(\text{CO}_2\) due to the decrease of the solvent density.
Conclusions

In conclusion, this work observed the opposite trend of extraction yield and anthocyanins content from *H. sabdariffa* calyces extract within the selected ranges of SC-CO$_2$ condition. The modifier effect was insignificant on anthocyanins content at 10 MPa. The solubility of *H. sabdariffa* calyces extracts ranged from 0.41 to 3.29 g/L in this study, and the Chrastil model was the most successful in correlating solute solubility when compared to the dVA and A-L models. The findings presented in this paper are the first steps toward developing more efficient extraction strategies and separation processes to obtain extracts with high anthocyanin concentrations from *H. sabdariffa* using SC-CO$_2$ (Figure 6). Higher pressure ranges must be observed to evaluate the actual effects of SC-CO$_2$ chemical parameters such as temperature and pressure.

Data availability

The datasets generated during and/analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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