Determination and modelling moisture sorption isotherms of dehydrated butterfly-pea (Clitoria ternatea L.) flower powder

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Abstract Butterfly-pea flower (Clitoria ternatea L.) is one of the edible flowers that is widely processed into dried flowers or powder form. Processed butterfly-pea flower is mostly used as a food colorant or flavonoid and anthocyanin-rich teas which are naturally present in the flower. Some polyphenolic acid, i.e., gallic acid, protocratic acid, and chlorogenic acid are also contained in this flower. During the storage period, color degradation occurs which will reduce the quality of the powder. Therefore, a study on the determination of moisture sorption isotherm from butterfly-pea powder is necessary information to maintain the quality of this product for a longer storage period. The objectives of this research are to evaluate the behavior of moisture sorption isotherm, construct its mathematical modelling and analyze the color changes at different temperatures and aw. 60 mesh of butterfly-pea powder with 28% initial moisture content (db) was stored at aw 0.3 – 0.9 (in a saturated salt solution containing MgCl₂, K₂CO₃, NaCl, KCl, and BaCl₂) at 30, 40, and 50°C by static gravimetric method. The results showed that based on the Brunauer classification, the behavior of moisture sorption isotherm of dehydrated butterfly-pea powder is in accordance with the Type II-sigmoid curve, while the Peleg model is the best model in predicting the moisture sorption isotherm. Recommended storage conditions for butterfly-pea flower powder are at 30°C with equilibrium moisture content at 23-30% (db). During storage powder color turns darker over the entire aw range with a color index of L* (lightness, 9.97); a* (redness, 2.33); b* (yellowness, -5.56).

1. Introduction
Butterfly-pea flower (Clitoria ternatea L.) is a legume plant that comes from the Fabaceae family. This plant is harvested at 42 days and reaches a range of 25-29 tonnes of dry matter/ha with seed production of 2.2 tonnes/ha [1]. The flower and leaf parts are generally used by the community as traditional medicine [2], natural food coloring, and beverages [3]. Butterfly-pea flower is a commodity that contains moisture content, ash, fat, protein, crude fiber, carbohydrates, minerals, and heavy metals [4], as well as bioactive compounds such as flavonoids and anthocyanins [5]. Anthocyanin compounds found in butterfly-pea flower extracts have high antioxidant activity compared to anthocyanins from other flower extracts [6].

Fresh pea flowers are perishable and have a short shelf life. Drying will facilitate the process of handling, storage and packaging fresh butterfly-pea flowers that are perishable and have a short shelf life. Drying will facilitate the process of handling, storage and packaging. However, during storage, the
color of the butterfly-pea flower may fade from initially blue-purple to pale purple. This corresponds to an increase in water content during storage. Wibowo et al. [7] reported that the discoloration occurred due to improper storage room conditions, such as temperature and humidity. Manolopoulou and Varzakas [8], revealed that color changes occur due to factors of water loss, changes in temperature, light, and humidity during storage. Therefore, it is necessary to study the determination of moisture sorption isotherm to determine the behavior of dehydrated butterfly-pea flower powder during storage at various conditions of temperature and $a_w$ (water activity). Recommendations for storage and drying through the water sorption isothermal approach have been successfully applied to modified cassava flour [9], cabya powder [10], milk-foxtail millet powder [11], and red pepper powder [12]. The objectives of this research are to evaluate the behavior of moisture sorption isotherm, construct its mathematical modelling, and analyze the color changes at different temperatures and $a_w$.

2. Materials and method

2.1. Raw materials and sample preparation
Fresh butterfly-pea raw material is obtained from Ajung District, Jember Regency, East Java with a moisture content of 12.64 (db) and then dried using a tray dryer at 50°C until it reaches a balance water content of 0.28 (db). The dried raw material is then crushed into 60 mesh powdered form as other commercial products available in the market. Most of the commercial butterfly-pea powders are sold in 60 mesh sizes and herbal powders are made in 60-80 mesh sizes [13]. Methods of preparation of desorption and adsorption samples as reported by Hawa et al. [10] for water sorption isothermal testing. For color change analysis using desorption samples.

2.2. Moisture sorption isotherm experiment
Conditioning $a_w$ storage 0.3 - 0.9 using a static gravimetric method with saturated salts of MgCl$_2$, K$_2$CO$_3$, NaCl, KCl, and BaCl$_2$. The placement and conditioning of water sorption isotherms on butterfly-pea powder refers to the method used by Hawa et al. [10], with a sample weight of 0.5 ± 0.001g. The storage temperature was set at 30, 40, and 50°C, as of moisture sorption isotherm determination. Mass data acquisition was carried out every 24 hours until equilibrium occurred three times (approximately after 5 days). The conditions of the research room ranged between 28-30°C and 74-78% relative humidity (RH).

2.3. Color change test
The color change is determined $L^*$, $a^*$, $b^*$ values with the image to analyze the overall color change in the sample during storage. Storage conditions are the same as the moisture sorption isotherm experiment. The image was taken using a Vario-Tessar ZEISS 3.3-6.3 / 4.5-36 20.1 MP lens and extracted the $L^*$, $a^*$, $b^*$ values using the help of the Matlab R2019a software (version 9.6.0.1072779), US. Color images were taken every 24 hours for 5 days. Each color parameter is represented by $L^*$ (lightness), $a^*$ (+ red to - green), and $b^*$ (+ yellow to - blue). The reference color for butterfly-pea flower powder is $L^* = 16.47$, $a^* = 3.33$, and $b^* = -8.81$ which is determined from butterfly-pea flower powder after blending.

2.4. Moisture sorption isotherm modelling
There are five moisture sorption isotherm models used in this study, namely Peleg, Oswin, Halsey, BET (Brunauer-Emmett-Teller), and GAB (Guggenheim-Anderson-de Boer) models. The constants C, K, a, b, n are constants in each equation model. The constant C in the Oswin Model is a linear function of temperature [11]. The BET model contains a constant Mo (monolayer capacity) and C (energy constant) [15], [16]. The GAB model contains constants C (corresponding to the heat region of the sorption monolayer) and K (associated with the heat region of the multilayer sorption) [15]. The results of the
equilibrium moisture content are then fitted using the nonlinear regression analysis to obtain the predictive value. The equations of the model used in the study are written below [17]–[20].

\[
EMC_{\text{(Peleg)}} = [a a_w^b + C a_w^n] \quad (1)
\]

\[
EMC_{\text{(Oswin)}} = \left[ C \left( \frac{a_w}{1-a_w} \right)^n \right] \quad (2)
\]

\[
EMC_{\text{(Halsey)}} = \left[ \left( \frac{C}{1-n a_w} \right)^{\frac{1}{n}} \right] \quad (3)
\]

\[
EMC_{\text{(BET)}} = \left[ \frac{M_a a_w}{(1-a_w)(1+(C-1)a_w)} \right] \quad (4)
\]

\[
EMC_{\text{(GAB)}} = \left[ \frac{M_o C a_w}{(1-K a_w)(1-K a_w+CK a_w)} \right] \quad (5)
\]

Statistical analysis is used to select the best mathematical model in predicting the water content of butterfly-pea flower powder equilibrium at various levels \( a_w \). The statistical analysis used is RMSE (root mean square error), \( P \) (mean relative modulus), and \( R^2 \) (coefficient of determination). The statistical analysis equation refers to Susilo et al. [21] and Hawa et al. [22].

3. Result and discussion

3.1. Water sorption isothermal modelling

The water content of butterfly-pea flower powder equilibrium in desorption and adsorption samples at 30, 40, and 50°C is shown in Table 1. The water content of the desorption sample's equilibrium was higher than the adsorption which indicated the occurrence of hysteresis.

| Desorption | 30 °C | 40 °C | 50 °C |
|------------|-------|-------|-------|
| Saturated salt solution | \( a_w \) | EMC | \( a_w \) | EMC | \( a_w \) | EMC |
| MgCl\(_2\) | 0.32 | 11.64 | 0.31 | 12.82 | 0.30 | 18.06 |
| K\(_2\)CO\(_3\) | 0.43 | 14.27 | 0.42 | 15.40 | 0.40 | 29.05 |
| NaCl | 0.75 | 25.87 | 0.75 | 30.99 | 0.74 | 35.02 |
| KCl | 0.83 | 39.58 | 0.82 | 45.05 | 0.81 | 58.76 |
| BaCl\(_2\) | 0.89 | 45.21 | 0.89 | 55.37 | 0.88 | 65.84 |
| Adsorption | 30 °C | 40 °C | 50 °C |
| -----------|-------|-------|-------|
| Saturated salt solution | \( a_w \) | EMC | \( a_w \) | EMC | \( a_w \) | EMC |
| MgCl\(_2\) | 0.32 | 11.36 | 0.31 | 12.50 | 0.30 | 17.87 |
| K\(_2\)CO\(_3\) | 0.43 | 13.82 | 0.42 | 15.05 | 0.40 | 28.85 |
| NaCl | 0.75 | 23.10 | 0.75 | 28.80 | 0.74 | 33.35 |
| KCl | 0.83 | 35.49 | 0.82 | 40.72 | 0.81 | 53.11 |
| BaCl\(_2\) | 0.89 | 44.02 | 0.89 | 53.75 | 0.88 | 63.77 |

Figure 1 depicted the relationship of water activity \( (a_w) \) with equilibrium moisture content (EMC). The higher the water activity made the equilibrium water content also increased. Based on Brunauer's classification, the moisture sorption isotherm of dehydrated butterfly-pea powder belongs to the Type II-sigmoid curve [23]. Type II Sigmoid has also been reported by Hawa et al. in modified cassava flour [9], cayba powder [10], kepok banana [21], and foxtail millet grain flour [24]. Generally, isothermal water sorption with high temperatures will affect the decrease in water balance [10], [17], [22].
molecule excitation state with increasing temperatures showed a higher equilibrium water content. This is caused by the tendency of the water molecules to be more mobile at higher temperatures, directly influencing the adsorption and desorption processes. However, in dehydrated butterfly-pea flower powder, the adsorption and desorption of water at higher temperatures showed a higher equilibrium water content. This is caused by the tendency of the water molecules to be more mobile at higher temperatures, directly influencing the mobility of the water molecules in the product and the dynamics of the equilibrium of the adsorption and desorption phases.

**Figure 1.** Hysteresis curve of dehydrated butterfly-pea flower powder, desorption prediction (black dot); adsorption prediction (red dot); desorption experiment (black); adsorption experiment (red) at (a) 30°C, (b) 40°C, (c) 50°C.

**Table 2.** Coefficients, constants, and statistics from GAB, BET, Halsey, Oswin, and Peleg Models.

| Sample  | Model | T (°C) | Model Coefficients | R² | P | RMSE |
|---------|-------|--------|--------------------|----|---|------|
|         |       |        | a       | b         | C    | K    | n    | M₀   |     |      |
| GAB     | 30    | -      | 11.006 | 0.876     | -    | 0.101| 0.983| 0.035| 0.016|
|         | 40    | -      | 8.745  | 0.899     | -    | 0.115| 0.991| 0.030| 0.014|
|         | 50    | -      | 662782.6| 0.880     | -    | 0.149| 0.909| 0.115| 0.050|
| BET     | 30    | -      | 11422710| -         | -    | 0.054| 0.933| 0.193| 0.051|
|         | 40    | -      | 5315860| -         | -    | 0.068| 0.956| 0.144| 0.047|
|         | 50    | -      | 3.46x10⁹| -         | -    | 0.090| 0.891| 0.185| 0.087|
| Halsey  | 30    | -      | 0.003  | -         | 0.128| -    | 0.935| 0.280| 0.065|
|         | 40    | -      | 0.004  | -         | 0.112| -    | 0.958| 0.242| 0.064|
|         | 50    | -      | 0.006  | -         | 0.134| -    | 0.893| 0.270| 0.109|
| Oswin   | 30    | -      | 0.139  | -         | 0.560| -    | 0.976| 0.090| 0.026|
|         | 40    | -      | 0.187  | -         | 0.526| -    | 0.989| 0.035| 0.016|
|         | 50    | -      | 0.280  | -         | 0.427| -    | 0.906| 0.108| 0.051|
| Peleg   | 30    | 0.147  | 0.195  | 0.526     | -    | 4.655| -    | 0.987| 0.041| 0.014|
|         | 40    | 0.164  | 0.210  | 0.699     | -    | 4.822| -    | 0.995| 0.029| 0.011|
|         | 50    | 0.813  | 7.256  | 0.372     | -    | 0.476| -    | 0.919| 0.113| 0.047|
| GAB     | 30    | -      | 1206542| 0.916     | -    | 0.079| 0.989| 0.038| 0.012|
|         | 40    | -      | 59.929 | 0.932     | -    | 0.092| 0.997| 0.017| 0.008|
|         | 50    | -      | 623594.9| 0.879     | -    | 0.142| 0.916| 0.104| 0.045|
| BET     | 30    | -      | 3931010| -         | -    | 0.051| 0.970| 0.180| 0.041|
|         | 40    | -      | 174510.2| -         | -    | 0.064| 0.980| 0.138| 0.037|
|         | 50    | -      | 228425.2| -         | -    | 0.085| 0.919| 0.183| 0.079|
| Halsey  | 30    | -      | 0.012  | -         | 0.585| -    | 0.987| 0.034| 0.013|
|         | 40    | -      | 0.019  | -         | 0.638| -    | 0.996| 0.017| 0.009|
|         | 50    | -      | 0.023  | -         | 0.513| -    | 0.920| 0.105| 0.043|
| Oswin   | 30    | -      | 0.151  | -         | 0.493| -    | 0.984| 0.050| 0.015|
|         | 40    | -      | 0.174  | -         | 0.536| -    | 0.994| 0.035| 0.011|
|         | 50    | -      | 0.269  | -         | 0.418| -    | 0.911| 0.103| 0.046|
| Peleg   | 30    | 0.566  | 6.196  | 0.160     | -    | 0.274| -    | 0.993| 0.035| 0.009|
|         | 40    | 0.202  | 0.402  | 0.713     | -    | 6.227| -    | 0.999| 0.017| 0.005|
|         | 50    | 0.908  | 8.613  | 0.362     | -    | 0.454| -    | 0.936| 0.014| 0.039|
In addition, there is a structural orientation to changes in temperature that expose polar bonds. Different hysteresis phenomena have also been reported in banana fiber, milk-foxtail millet powder, and mint leaves under several conditions of water activity.

Coefficients, constants, and the results of statistical analysis in the form of $R^2$, $P$, and RMSE in the GAB, BET, Halsey, Oswin, and Peleg models are shown in Table 2. From these 5 models, it is found that the Peleg model is the best model that can describe the behavior of moisture sorption isotherm of dehydrated butterfly-pea flower powder in the range $a_w$ 0.3-0.9.

3.2 Color changes
Dehydrated butterfly-pea flower powder discoloration occurs during storage. In Figure 2 the desorption sample increases in total color difference ($\Delta E$) and yellowness ($b^*$) and decreases in lightness ($L^*$) and redness ($a^*$) at $a_w$ 0.32 - 0.90.

The change in visualization brightness ($L^*$) for 5 days of storage is shown in Figure 3. At the beginning of storage, the color of dehydrated butterfly-pea flower powder was purplish-blue with a brightness index of 15.69 and at the end of storage, it turned blackish blue. At a longer storage period, the color of dehydrated butterfly pea flower powder was darker along storage time. $L^*$ value at the end of storage at $a_w$ of 0.32, 0.43, 0.75, 0.84, and 0.9 were 6.95, 6.79, 6.68, 6.09, and 6.01, respectively.

Generally, the color change is influenced by temperature and $a_w$ factors, the presence of an oxidation reaction, non-enzymatic browning, and glass transition. According to Mosquera et al. [25], $a_w$ 0.43 is expressed as the starting limit for the increase in the enzymatic browning reaction. The phenomenon of increasing and decreasing parameters $\Delta E$, $L^*$, $a^*$, $b^*$ has also been reported on red pepper powder using the static gravimetric method [12]. The results of their report have similarities with this study, because $a_w$ and temperature affect the color change. The color change at high water activity causes the product to darken due to enzymatic reactions and is associated with changes in the hue angle and chroma angle which causes a decrease in the value of lightness [12].
The recommendation for storing butterfly-pea flower powder is at a temperature of 30 °C, $a_w$ 0.32 and equilibrium water content of 23-30% (db) because at low $a_w$ the color can be preserved. This recommendation refers to Mosquera et al. [30] on borojo fruit storage at $a_w$ 0.32 and Tellis et al. [31] on grapefruit juice powder at $a_w$ 0.32.

4. Conclusions
Hysteresis occurs on the moisture sorption curve of the moisture sorption isotherm of dehydrated butterfly-pea flower powder where the desorption curve is higher than the adsorption curve. Based on the Brunauer classification, the moisture sorption isotherm behavior corresponds to the Type II-sigmoid curve. Peleg’s model is the best model that can predict the equilibrium value of water content. The color of the dehydrated butterfly-pea flower powder became darker at the end of storage as indicated by an increase in total color ($\Delta E$) and yellowish index ($b^*$) as well as a decrease in brightness ($L^*$) and redness index ($a^*$). The recommended storage conditions for dehydrated butterfly-pea flower powder at 30°C, $a_w$ 0.32 and equilibrium water content of 23-30% (db).

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