Moisture Sorption Isotherm and IsostERIC Heat of Dried Cabya (*Piper retrofractum* Vahl) Powder

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Abstract. Cabya (*Piper retrofractum* Vahl) is a widely utilized herbal plant for Indonesian traditional medicine. Up to date, the commonly applied storage method for this plant is in dried form, and makes it less effective for distribution process and less attractive for consumers preference, i.e. consumers usually prefers to consume herbal product in powdered form. In the attempt to provide an optimized storage condition of dried cabya powder, the study was conducted to analyze the sorption isotherm behavior of dried cabya powder and to obtain the fittest sorption isotherm model by comparing obtained data to five commonly used sorption isotherm models, i.e. BET, Oswin, Smith, Caurie, and GAB model. The sorption isotherm data was obtained using static gravimetric method in 24 h of interval weighing observation. Six saturated salt solution, i.e. KOH, MgCl₂, KI, NaCl, KCl, and KNO₃ were employed for water activity (a_w) in the range of 0.063 – 0.936. The observation was conducted at three different temperatures, i.e. 25±2°C, 35±2°C, and 45±2°C with triplicates. The results indicated that GAB model satisfactorily describe the sorption isotherms behavior of dried cabya powder. The mathematical form of isosteric heat equation of dried cabya powder in adsorption and desorption were also presented.

Keyword: dried cabya powder; *Piper retrofractum* Vahl; mathematical models; isosteric heat

1. Introduction

Indonesia is popularly recognized as a country with high natural diversity, with one of species that beneficial and widely used is cabya (*Piper retrofractum* Vahl) or also known as Javanese long pepper. It commonly used as traditional medicines in Indonesia [1]. Numerous researches have been conducted to explore the benefit of the fruits, i.e. antifungal, antibacterial [2], and anti-obesity agent [3]. The most common postharvest practices for the fruit in Indonesia is the fruit dried using traditional open sun drying [1] in the form of whole fruit, which is less effective in the distribution process and less attractive for consumers preference, i.e. consumers usually prefers to consume herbal product in powdered form.

However, the powdered form of agricultural product is prone to deterioration in terms of quality if not stored and packaged properly. In general, agricultural products can absorb and release water content in the environment, called as the hysteresis pattern. The relationship between water activity in materials and relative humidity of environment is referred as moisture sorption isotherms [3]. The moisture sorption isotherm is the relationship between moisture content of product and water activity of the environment at certain range of values, observed at constant temperature under equilibrium condition and expressed graphically [4].
Currently, series of studies regarding several methods of cabya fruit drying process and its further postharvest processing is extensively conducted at Department of Agricultural Engineering, Universitas Brawijaya, Indonesia. Due to various benefits of cabya fruit and its huge potential in dried powdered form for development of a new traditional refreshment product, the further research regarding its behavior is mandatory, i.e. moisture sorption isotherm and isosteric heat. The objective of present study was to determine and quantify moisture sorption isotherm of dried cabya powder at three different temperatures, i.e. 25±2°C, 35±2°C, and 45±2°C with standard gravimetric method, and to model the moisture sorption isotherm data using selected commonly used equations. In addition, the mathematical form of isosteric heat equation of dried cabya powder in adsorption and desorption were also investigated.

2. Methods

2.1. Material preparation

The fresh cabya fruit obtained from farmers in Jember, East Java Province, which harvested at the orange edible maturity stage (Fig. 1) with 68.57±2.20% of average moisture content according to standard gravimetric method, 4.4±2 cm of length. The fruit then cleaned from the dust and excessive peduncles, blanched in hot water at 80°C for 10 minutes and then dried using forced convective hot air dryer at 50°C for 24 h until it reach 10.00±0.5% (wb) of average moisture content. The dried cabya fruit then size reduced using food processor for 3 minutes. Five standard saturated salts, namely potassium hydroxide (KOH), magnesium chloride (MgCl2), KI (potassium iodide) potassium nitrate (KNO3), sodium chloride (NaCl), and potassium chloride (KCl) were also purchased from local provider (PT. Panca Adi Aneka Kimia, Indonesia). The saturated salts used allowing the obtaining of water activity (a_w) values ranging from 0.063 to 0.936.

Figure 1. The orange edible maturity stage of cabya fruit.

2.2. Moisture sorption isotherm determination

The gravimetric static method were used to obtain adsorption and desorption isotherms data of dried cabya powder at three subjected temperature (25±2°C, 35±2°C, and 45±2°C) as commonly used for agricultural-based products. The experimental procedure consists of five hermetic jars of 0.5 l each. Two disposable cups were inserted into the container. The first cup was filled with a prepared standard saturated salt solution (20 ml) and the second cup was filled with the dried cabya powder sample (1±0.1 g). Triplicate dried cabya powder of 1±0.1 g for both adsorption and desorption experiments were weighted. Native dried cabya powder was used for desorption experiments. Dried cabya powder samples used for adsorption isotherms were dehydrated for 72 h in an oven at 50°C and then placed in desiccators with silica gel for 48 h.

The sample then placed in the jars, and closed tightly and placed in temperature controlled incubator. The incubator previously allowed to be running empty for 2 h to enable it steadied at a
subjected temperature (25±2°C, 35±2°C, and 45±2°C) in order to maintain a constant relative humidity corresponding to a constant water activity ($a_w$) of the powder for respective temperature. The powder samples were weighted manually every 24 h using digital balance with ±0.001 g of accuracy. The observation was concluded when three successive weight measurements showed a difference of less than 2%, and the equilibrium moisture contents ($X_e$) of samples were measured.

2.3. Mathematical modeling of sorption isotherms
For sorption isotherms modeling, the final dry basis moisture contents of the samples were used. The experimental data were regressed to five mathematical models summarized in Table 1 using Microsoft Excel 2010 (Microsoft, USA). Three statistical parameters were used to evaluate the ability of subjected model to fit the experimental data, namely the mean relative percent error ($P$), the standard error ($SE$) and the coefficient of determination ($R^2$) between the experimental and the predicted data.

![Table 1](image)

2.4. Isosteric heat determination
The isosteric heat of adsorption and desorption of dried cabya fruit powder was estimated using Eq. 1 which derived from Clausius-Clapeyron equation fixed moisture contents, where $q_{st,n}$ represent isosteric heat of sorption (kJ/mol), $a_w$ is water activity, $T$ is absolute temperature (K), $R$ is the universal gas constant (kJ/mol K) and $K$ is a constant [5].

$$\ln(a_w) =\left(\frac{q_{st,n}}{R}\right)\left(\frac{1}{T}\right)+K$$

(1)

3. Results and Discussion
3.1. Moisture sorption isotherm of dried cabya powder
Figure 2 indicates the effect of temperature on sorption isotherms of dried cabya powder, with higher temperature slightly lead to lower equilibrium moisture contents ($X_e$). According to Brunauer et al. [6], the sorption isotherms curve was grouped into five types and the results of present study has type II sigmoid curve. This classified also found at other products such as lemon juice [7], lemon peel [8] and banana var. Raja Nangka [9]. Fig. 2 also revealed that there was no significant moisture sorption hysteresis was found for all subjected temperatures. The moisture sorption hysteresis is the phenomena by which two different paths are found between the adsorption and desorption isotherms.

As depicted in Table 2, the fittest model to describe the relationship between the equilibrium moisture content of dried cabya powder and water activity was the GAB (Guggenheim-Anderson-de
Boer) model. It can be shown that the GAB model provides the best fit to experimental data of both adsorption and desorption isotherms of dried cabya powder for wide range of water activity at all subjected temperatures. GAB model was chosen since the only model that has lowest $P$ value for both adsorption and desorption isotherms and also has highest $R^2$ and the lowest $SE$. In GAB model, there are three kinds of constants, which are $X_m$, $A$ and $B$. The constant $X_m$ is the value of the monolayer water content on the material. The $A$ and $B$ are constant related to the energies of interaction between the first and further molecules at the individual sorption sites. The model has several advantages than other model since it has viable theoretical background, as well as all parameter constants in the model have physical meaning [10].

Table 2 shows that the best model to describe the relationship between the equilibrium moisture content and water activity is the GAB (Guggenheim-Anderson-de Boer) model. The theoretical basis for absorption of the GAB model is the assumption of multilayer water bonds, including: the first water layer evenly covers the sorbent surface, bonded in a monolayer and subsequent water layers which less interact with the sorbent surface [11] [12].

![Figure 2. The moisture sorption isotherm curve of dried cabya powder. Experimental adsorption data (red dot); Experimental desorption data (black); Predicted data (line)](image)

| Model Name | Temperature(°C) | Desorption | | | Adsorption | | |
|---|---|---|---|---|---|---|---|
| | | $R^2$ | $P$ | RMSE | $R^2$ | $P$ | RMSE |
| BET | 25 | 0.94 | 35.46 | 5.85 | 0.92 | 36.95 | 5.83 |
| | 35 | 0.94 | 27.94 | 4.54 | 0.94 | 27.13 | 4.87 |
| | 45 | 0.98 | 11.59 | 1.55 | 0.97 | 10.52 | 1.66 |
| Oswin | 25 | 0.99 | 7.86 | 0.94 | 0.99 | 6.98 | 0.90 |
| | 35 | 0.99 | 7.64 | 0.98 | 0.99 | 7.94 | 0.86 |
| | 45 | 0.98 | 11.18 | 1.13 | 0.97 | 12.91 | 0.01 |
| Smith | 25 | 0.97 | 11.29 | 1.57 | 0.98 | 9.29 | 1.44 |
3.2. Isosteric heat

Experimental sorption isotherms of dried cayapa powder were used for isosteric heat determination. Predicted sorption isotherms by GAB model for each temperature were used to obtain water activities ($a_w$) values by interpolation at different experimental temperatures for constant moisture content. Fig. 3 depicted the variation of isosteric heats of sorption for different equilibrium moisture content ($X_e$).

As revealed in the figures, the isosteric heat of sorption was high at lower moisture content and then decreased at high moisture content. At lower moisture content, the higher isosteric heat might caused by the greater resistance to movement of water from interior to the surface of the powder [5]. It also can be seen that the isosteric heat of desorption is slightly higher than that of adsorption. This phenomenon indicates that the energy needed in desorption process is higher compared to adsorption. The absorption of isosteric heat on almond will decrease in value as the water content in the material increases [13]. Isosteric heat has a higher value at lower water levels due to greater resistance to water movement from the inside to the surface of the sample [14]. In addition, the pre-drying for adsorption sample might also contribute for the differences of isosteric heat of adsorption and desorption for dried cayapa powder. $q_{st}$ value becomes negative due to purely mathematical calculations, not due to the determination error [15].

$$ q_{st} = 73.5506 \exp \left[ -\frac{X_e}{5.26072} \right] \quad (2) $$

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|       | 35  | 0.97 | 10.67 | 1.44 | 0.97 | 11.28 | 1.79 |
|-------|-----|------|-------|------|------|-------|------|
|       | 45  | 0.96 | 9.29  | 1.07 | 0.95 | 10.13 | 1.27 |
| Caurie| 25  | 0.94 | 21.6  | 2.82 | 0.96 | 19.69 | 2.57 |
|       | 35  | 0.95 | 19.25 | 2.43 | 0.95 | 19.74 | 2.63 |
|       | 45  | 0.95 | 14.22 | 1.45 | 0.94 | 15.02 | 2.10 |
| GAB   | 25  | 0.99 | 3.65  | 0.66 | 0.99 | 2.57  | 0.39 |
|       | 35  | 0.99 | 3.47  | 0.65 | 0.99 | 3.98  | 0.58 |
|       | 45  | 0.99 | 3.13  | 0.58 | 0.98 | 6.63  | 1.06 |
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\[ q_{st} = 51.9358 \exp \frac{-X}{6.45602} \]

4. Conclusion
The sorption isotherms of dried cabya powder were examined at three temperatures (25±2°C, 35±2°C, and 45±2°C) using standard gravimetric method. Both adsorption and desorption isotherms of dried cabya powder have a sigmoid form with type II according to BET classification. In all temperatures examined, no significant moisture sorption hysteresis was found. GAB model was in good agreement for the prediction of the adsorption and desorption isotherms of dried cabya powder in all subjected temperatures with water activity ranging from 0.063 to 0.936. The isosteric heat of sorption increased with decreasing moisture content and the heat of desorption process is slightly higher than that of adsorption.

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