Moisture Adsorption Isotherm of Dried Cassia alata Herbal Leaves at Different Temperatures

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Abstract. Moisture adsorption isotherm study of dried Cassia alata was evaluated in this work. Adsorption isotherm of dried C. alata was determined at three different temperatures (10, 30 and 40 °C) and at six levels of relative humidity (ranging from 23 to 87%) using a gravimetric technique. The sorption isotherms were found to be typical type II sigmoid. The experimental data obtained was fitted to several mathematical models viz. two-parameter (BET, Oswin, Smith, Caurie, and Iglesias and Chirife), and three-parameter (GAB) relationships. Standard statistical procedures were applied to deduce percent error (P), root mean square error (RMSE) and coefficient of relation ($r^2$). In terms of the mean absolute percentage error (P) of the fits, those with less than 10% error can be considered acceptable and an $r^2$ of >0.98 may also indicate a good fit. The Peleg followed by Iglesias and Chirife model were found to best fit the experimental data.

1. Introduction
Cassia alata (gelenggang) is one of the prioritized Malaysian herbal species. It is an herbaceous shrub originated from Central America but has been introduced into many tropical countries including Malaysia [1] The C. alata leaves are yellowish-green, broad, with 5–14 leaflet pairs. It grows well in sunny and moist areas. Traditionally, C. alata has been used as a laxative by drying the leaves and then made it as tea. Besides that, C. alata leaves has been known as the remedy for ringworm, eczema, poisonous bites and several other skin diseases. The remedial value in C. alata is due to its phytochemical compounds and antimicrobial activity [2] Once harvested, the leaves are dried and stored for further processing into medicinal pharmaceutical products.

The most common preservation method for medicinal plants is by drying. The common method used for drying are such as sun drying, oven drying and freeze drying. The main purpose of drying is to reduce the moisture content for conserving medicinal qualities of herbs and to preserve materials over prolonged periods. Appropriate moisture level is important to slow down the bioactive compounds degradation as well as to stop microbial growth during storage [3]. It is a common practice dried herbs are packed and stored for a certain period of time before it goes through downstream processing into herbal medicinal and pharmaceutical products.

The physical and chemical parameters along with microorganism growth determine the quality of medicinal dried herbal materials during storage. Water, temperature, packaging material and light are among the factors affecting dried herbs quality stability. However, among these factors water is known

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to have most impact in preservation of herbal material. As of other biological materials, the quality of preserved herbal materials depends on dynamic movement of water through adsorption and desorption mechanism. This mechanism is normally expressed as a relationship between equilibrium moisture content (EMC) of the food material and its water activity (aw), at constant temperature. The EMC increases with increase in relative humidity and on the other hand decreases with increase in temperature. This relationship between EMC and corresponding relative humidity at constant temperature is described as moisture sorption isotherm.

Moisture sorption isotherms are specific for each biological material and are important for drying processes modelling, drying equipment design, calculation of moisture changes during storage, prediction of shelf-life stability, and selecting appropriate packaging materials [4]. Numerous mathematical models are now available that can be applied for predicting moisture sorption properties of agricultural materials. These moisture sorption isotherms models can be grouped as theoretical, semi-empirical and empirical. In some ranges of water activity, sorption isotherms can be approximated to linear equations. There are some semi-empirical equations with two or three fitting parameters to describe moisture sorption isotherms. From the literature search, there are several models that have been used to establish the moisture sorption of herbs. The most commonly used moisture sorption isotherm models for dried herbs are such as Oswin, Peleg, Iglesias and Chirife, Caurie, GAB (Guggenheim-Anderson-de Boer, BET (Brunauer–Emmett–Teller), Halsey and Modified Oswin. Nevertheless, no single model is precise enough to represent all the sorption isotherms of all products [5].

It is a standard practise that a freshly harvested C. alata leaves are sun-dried or oven dried. The dried leaves are normally packaged in plastic bags and stored for a certain period of time before transported to processing plant local and overseas. Quality maintenance and transportation during storage will affect the products. It has been mentioned earlier that water activity and temperature plays a major role in preserving the quality of herbal products. There is scarce information on optimum water activity of leaves during storage. The general goal of this study is to find a suitable moisture content in dried leaves of C. alata for storage purpose. Therefore, the objectives of the study were (i) to investigate the moisture adsorption behaviour of C. alata leaves at temperatures typically found in storage and processing of medicinal plants (ii) to find the most appropriate mathematical model to describe the experimental adsorption data.

2. Materials and Methodology
2.1. Plant material
C. alata plants were grown at the Universiti Malaysia Perlis (UniMAP) Agrotechnology Research Station, Sg. Chucuh, Perlis, Malaysia. The plants were grown from cuttings and maintained according the standard practiced adopted by the majority growers in Malaysia.

2.2. Determination of adsorption isotherm
In this experiment, adsorption isotherm of dried leaves was determined. For the experimental purpose, the freshly harvested leaves, uniform with similar maturity of C. alata were oven-dried at 40°C for 48 hours. Each dried leaf was cut into 3 pieces and randomly mixed in a container. Sample size of about 0.5g of dried leaves were weighed and placed in a clean and dry glass petri dishes. The samples were prepared in replicates of four at each temperature and each ERH levels. All petri dishes were placed on ceramic plate inside desiccators containing salt solutions. The desiccators were tightly closed using grease and were placed in a cooler at 10°C and at cabinet dryers of temperature 30 and 40°C. Table 1 shows the list of chemicals that were used for this study.

The weights of the samples in the desiccators were taken by using an analytical balance every two days until they reach equilibrium stage. The weight of the samples were considered to achieve equilibrium where the difference between three consecutive readings is less than 0.001g. The final moisture content of C. alata leaves were determined by drying in the oven at 105°C for 24 hours. Equilibrium moisture content (EMC) of the samples were calculated using the following equation:
\[ EMC_{(d,b)} = \frac{w_f - w_{dm}}{w_{dm}} \]  

(1)

| Salt solution  | Relative Humidity (%) |
|----------------|-----------------------|
| Potassium acetate | 23                    |
| Magnesium chloride | 33                    |
| Sodium bromide     | 54                    |
| Sodium nitrite      | 65                    |
| Sodium chloride     | 75                    |
| Potassium chloride  | 87                    |

Table 1. The saturated solution with its relative humidity.

2.3. Modelling of adsorption isotherm

Mathematical modelling were carried out to fit the experimental data to predict the EMC of *C. alata* leaves. Six widely used sorption models for agricultural produces, namely Oswin, Guggenheim-Anderson-de-Boer (GAB), Peleg, Iglesias and Chirife, Caurie and Modified Oswin models were used in developing the moisture adsorption isotherms. The equation of each model is listed in Table 2.
Table 2. Mathematical modelling for moisture sorption isotherms.

| Models                        | Equation                                      | Eq. No |
|-------------------------------|-----------------------------------------------|--------|
| Oswin                         | $EMC = k \left( \frac{a_w}{1-a_w} \right)^n$ | 2      |
| Peleg                         | $EMC = k_1 a_w^{n_1} + k_2 a_w^{n_2}$         | 3      |
| Iglesias and Chirife          | $EMC = A + B \left( \frac{a_w}{(1 - a_w)} \right)$ | 4      |
| Caurie                        | $EMC = \exp(A + B . a_w)$                     | 5      |
| GAB                           | $EMC = \frac{M_0 C k a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$ | 6      |
| Modified Oswin                | $EMC = (A + B . T) \left( \frac{a_w}{1 - a_w} \right)^c$ | 7      |

The SPSS software version 23 was used to perform a nonlinear regression analysis in order to evaluate the constant parameters of the sorption models, as listed in Table 2. The polynomial form of GAB model was used to evaluate the constant parameters and the monolayer moisture content ($M_0$) values using Microsoft Excel 2013 software. These constant parameters and monolayer moisture content deduced from both models were then used as initial values in the nonlinear regression analysis. As for Oswin, Peleg, Iglesias and Chirife, Caurie and Modified Oswin models, the initial values were guessed using ‘trial and error’ method, since these models were less complicated as compared to GAB model.

3. Results and Discussion
3.1. Experimental adsorption isotherm

Moisture adsorption behaviour of *C. alata* leaves were determined at three temperature levels of 10, 30 and 40°C, and six relative humidity (RH) levels that ranged from 23 to 87%. The curve of equilibrium moisture content (EMC) against equilibrium relative humidity (ERH)/water activity ($a_w$) is a sigmoid type (Figure 2). The results show that, the equilibrium moisture content (EMC) increased as the water activity increased. The results also showed the EMC of dried *C. alata* leaves decreases with increase in temperature at a constant $a_w$. For instance, the EMC of sample is higher for 10°C as compared to 30 and 40°C. Similar results have been reported by various workers working on different types of agricultural materials. For instance, for $a_w$ less than 0.7, higher temperature resulted in lower the equilibrium composition of cassava (*Manihot esculenta*) leaves [6]. Similarly, the equilibrium moisture content (EMC) of Moroccan rosemary leaves has been shown to increase as the temperature decreases [7]. The association of EMC and temperature might be caused by the excitation states of water molecules of the experimental samples. As the temperature increases, the excitation of water molecules increases, which causes an increase in the distance between the molecules and decreases the attractive forces between them [8]. This leads to a decrease in the degree of water sorption at a given water activity, as the temperature increases [9].
As has been mentioned earlier, the experimental adsorption isotherm of *C. alata* leaves exhibited sigmoid pattern. It is most likely that the Brunauer, Emmet and Teller (BET) moisture sorption isotherm Type II. Type II and Type III are common for agricultural produce. This is in agreement with findings on other herbal species. For instance, a similar trend of Type II adsorption isotherm was also reported for Moroccan rosemary leaves at temperatures of 30, 40 and 50°C [7] and dry persimmon leaves at temperatures of 20, 30 and 40°C [10]. However, some other leaves were reported to exhibit the Type III BET classification. For instance, the moisture sorption isotherm of *Orthosiphon stamineus* leaves and orange leaves and peel [11] [12].

### 3.2. Modelling of adsorption isotherm

The purpose of mathematical modelling of moisture adsorption isotherm is to determine the best fit water activity for quality preservation during storage. Mathematical modelling was performed using nonlinear regression analysis to predict models constant parameters for moisture adsorption isotherm at the studied conditions. The constant parameters were then used to calculate the predicted data. Then the experimental data obtained were compared with the predicted data. The best fit model was selected based on standard statistical evaluation.

Moisture sorption isotherms models used were Oswin, Guggenheim-Anderson-de-Boer (GAB), Peleg, Iglesias and Chirife, Caurie and Modified Oswin models. Standard statistical procedures were applied to deduce percent error (P), root mean square error (RMSE) and coefficient of relation (r²). In terms of the mean absolute percentage error (P) of the fits, those with less than 10% error can be considered acceptable (Foster, Brolund & Paterson, 2005) and an r² of >0.98 may also indicate a good fit.
Table 3. Adsorption isotherm model parameters for *C. alata* dried leaves at 10, 30 and 40 °C.

| Model                  | Temp. (°C) | Fitting criteria | Constants |
|------------------------|------------|------------------|-----------|
|                        |            |                  |           |
|                        | 10         | 0.9974           | 0.0117    | 10.7724  | 0.0970 | 0.6220 |
| Oswin                  | 30         | 0.9975           | 0.0139    | 14.3408  | 0.0780 | 0.6390 |
|                        | 40         | 0.9959           | 0.0209    | 26.5281  | 0.0630 | 0.6970 |
|                        | 10         | 0.9999           | 0.0044    | 3.6634   | 0.5170 | 6.3490 | 0.1140 | 0.3930 |
| Peleg                  | 30         | 1.0000           | 0.0081    | 6.1509   | 0.4330 | 5.5820 | 0.0710 | 0.1780 |
|                        | 40         | 0.9998           | 0.0146    | 13.5449  | 0.3960 | 4.0950 | 0.0140 | -0.8610 |
| Iglesias & Chirife     | 10         | 1.0000           | 0.0047    | 3.4652   | 0.0550 | 0.0400 |
|                        | 30         | 1.0000           | 0.0104    | 5.9041   | 0.0430 | 0.0340 |
|                        | 40         | 0.9996           | 0.0200    | 17.3448  | 0.0310 | 0.0310 |
|                        | 10         | 0.9950           | 0.0197    | 17.1696  | -4.0290| 3.2630 |
| Caurie                 | 30         | 0.9950           | 0.0188    | 20.6324  | -4.3240| 3.3970 |
|                        | 40         | 0.9921           | 0.0215    | 30.2483  | -4.8170| 3.8570 |
|                        | 10         | 0.9991           | 0.1359    | 2.9497   | -38.0200| 0.9903 | 0.0457 |
| GAB                    | 30         | 0.9941           | 0.1132    | 7.1824   | -19.6624| 1.0016 | 0.0351 |
|                        | 40         | 0.9376           | 0.1184    | 14.7460  | -7.6112| 1.0604 | 0.0221 |
|                        | 10         | 0.9977           | 0.0131    | 11.4545  | -0.0700| 0.0170 | 0.6220 |
| Modified Oswin         | 30         | 0.9986           | 0.0215    | 17.9070  | -1.2630| 0.0540 | 0.6390 |
|                        | 40         | 0.9932           | 0.0326    | 27.7214  | -1.3100| 0.0340 | 0.6970 |

The results of fitting criteria values, as tabulated in Table 3 for the selected sorption models, showed all the values were within the acceptable range. The Peleg model had shown excellent performance for adsorption isotherm for all temperatures as compared to the other models. The model had the highest values of $r^2$ (0.9998 to 1.000), and the lowest values of RMSE (0.0011 to 0.0146) and P (0.9581 to 13.5449%). On the other hand, Iglesias and Chirife model depicted the second best performance with $r^2$ of 0.991 to 1.000, RMSE of 0.0047 to 0.0137 and P of 3.4652 to 17.3448%. On the other hand, GAB model produced the least fitting criteria, as shown in Table 5.4e. The $r^2$ values ranged from 0.9376 to 0.9995, the RMSE values were from 0.0707 to 0.1359 and the P values were 1.2687 to 14.746%.

Furthermore, the Peleg model established that *C. alata* is useful in facilitating interpolation of the final moisture content at known drying and storing conditions (temperatures of 10, 30 and 40°C and relative humidity ranged from 23 to 87%). For example, at storage conditions of 30°C and humidity level of 40%, with the predicted Peleg constants as shown in Table 5.4b, the final moisture content safe for storage is 0.0775 g water/ g dry matter.
4. Conclusion
The equilibrium moisture content of *C. alata* leaves at three temperatures and six relative humidity levels in the range of 23–87%, were determined. From the results, it is concluded that the sorption isotherms of medicinal plants can be measured by a gravimetric static method with sufficient accuracy for practical purposes. The experimental data were used to determine the best model for predicting the adsorption isotherm of dried *C. alata* leaves for known levels of temperature and relative humidity. Mathematical models that best fitted the experimental data were found by statistical analysis of the experimental data: the Peleg model.

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