# MOISTURE ADSORPTION ISOTHERMS OF ASSAM GREEN TEA POWDER

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## Abstract

Moisture adsorption isotherms of Assam green tea powder were determined at 25, 35 and 45°C. A water activity analyzer (Novasina® model LabMaster-$a_w$) was used to detecting the equilibrium over the relative humidity range of 30-70%. The sorption isotherms of Assam green tea powder were typical type III sigmoid curves, according to BET classification. The equilibrium moisture content data were fitted to six mathematical models. From the estimated parameters of different models, it was indicated that the Peleg model gives the best fit to the experimental data and it is the most suitable model for describing the relationships between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) of Assam green tea powder over the entire range of temperature. The net isosteric heat of sorption was determined by the Clausius-Clapeyron equation and was found to be between 45.2 and 45.6 kJ/mol at moisture levels ranged 0.05-0.25 g/g dry matter.

**Keywords** : Assam green tea powder, adsorption isotherm, isosteric heat of sorption, equilibrium moisture content.

## Introduction

The northern part of Thailand is the major tea growing area and includes the provinces of Chiangrai, Chiangmai, Lampang, Phrae and Mae Hong Son. One notable tea growing area is Doi Mae Salong in Chiangrai where there is a tea plantation of 4,500 rais. Different kinds of tea are produced here, and the province of Chiangrai produces about 200 tons of tea a year. About 70% of the tea production is consumed in Thailand, while the other 30% is exported. Much of the tea produced in Thailand is Assam tea which is the local plant of the northern part. Assam tea production has a high volume of 83% and 17% for Chinese tea (Department of Agricultural Extension Thailand, 2003).

There are many kinds of tea and tea products and one interesting product is 'instant tea' or 'tea powder'. It is widely used for application in the ingredients of food, snacks, beverages, cosmetics and drugs. Instant green tea is one of the most widely consumed beverages worldwide because of its aroma, stimulatory effect, health benefits and convenience in use (Sinija and Mishra, 2008). Because of its processing, instant tea decreases the transportation and storage costs due to a decrease in weight and volume. In addition, value added and prolonged shelf-life are interesting points for the manufacturer.

The moisture sorption isotherms of the tea powder are very useful for predicting its stability during storage and selecting appropriate packaging materials (Sinija and Mishra, 2008). Moisture sorption isotherms show the relation between water activity and change in moisture content of a sample at a specified temperature. Brunauer et al. (1940) classified adsorption isotherms into five general types. Type (I) represents a characteristic increase in water activity with increasing moisture content and this type is useful for filling the water monomolecular layer at the internal surface of a material. Type (II) represents the sigmoidal model as though BET or GAB equations and it is useful for the existence of multilayer at the internal surface of a material. In addition, type (III) of isotherms are relatively rarely observed and can be found in the case of solids soluble in water e.g., salt or sugar. Type (IV) and (V) are more complicated sorption isotherms which are normally observed in the case of capillary condensation (Blahovec and Yanniotis, 2009).

Few studies have been done on the moisture sorption isotherms of Assam green tea powder. Therefore, this study was carried out with the objectives of studying the moisture sorption characteristics of Assam green tea powder and investigating the most suitable model for describing the isotherms of Assam green tea powder. Finally, this study was also made to calculate the net isosteric heat of sorption from the experimental data.

## Methodology

1. Preparation of samples

Dried Assam green tea leaves (*Camellia Sinensis* var. *assamica*) were purchased locally in Chiangrai, Thailand. The dried tea leaves were ground using a hammer mill equipped with a 5 mm sieve. The extraction apparatus illustrated in Figure 1 was used to extract the ground tea leaves to obtain tea extract. In tank no.1, seven liters of acidified water (pH 5.0) were heated up until the temperature of the water reached 90 °C. Thereafter, 250 g of ground tea leaves with moisture content of 7.63% (d.b.) was placed into tank no.2 of the extractor for 80 minutes. The liquid was filtrated through a cloth sheet and the extract was kept in a cold room (4 °C). The tea extract with a total solid content of 0.8-1% was subjected to the Flash Evaporator (Figure 2) with an evaporating temperature of 70 °C to obtain concentrated tea extract with a total solid content of 20-25%. A pilot plant spray dryer (GEA NIRO, Copenhagen Denmark) was operated as co-current flow. The speed of the feeding pump was set at 8 rpm corresponding to a 1 kg/hr feed rate and the pressure of compressed air was manipulated at 3 bars (10.8 kg air/hr). The inlet air temperature was controlled at 180 °C (Wongsuwan, 2008). The product was collected in a glass jar connected to a cyclone. Then, it was kept over dried silica gel until used in the experiment.

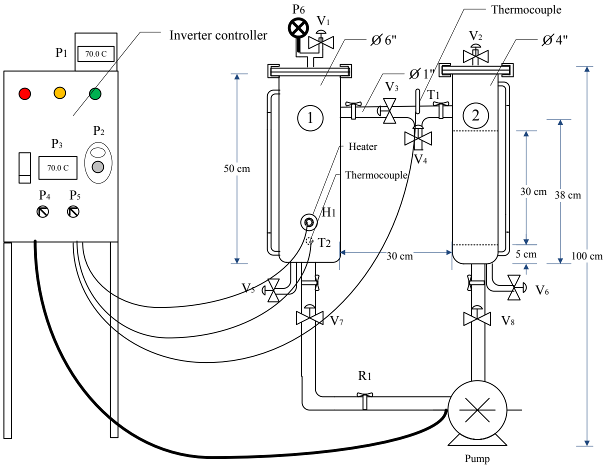


**Figure 1** Schematic diagrams of a solid-liquid extraction apparatus

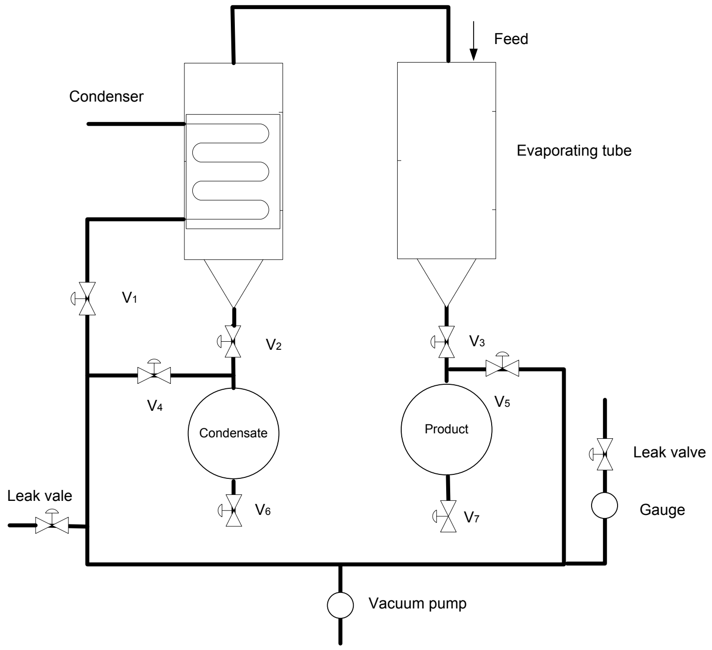


**Figure 2** Schematic diagrams of a Flash Evaporator

2. Moisture adsorption isotherms

For the study of adsorption isotherms, saturated salt solution (lithium chloride, magnesium chloride, magnesium nitrate, sodium chloride, potassium chloride and potassium nitrate) were used for maintaining equilibrium relative humidity (ERH) levels from 10% to 90%. A water activity analyzer, the Novasina® model LabMaster-aw (Axair Ltd., Switzeland) instrument was used for detecting the equilibrium. Place the standard saturated salt solution into a detector chamber of water activity analyzer and set the chamber temperature at the desired value. Empty sample containers were dried in a hot air oven and the weight after drying was recorded. The sample (approximately 1 g) was placed above the selected saturated salt solution until it became equilibrial with the salt solution. The equilibrium was reached when the change in value of water activity and temperature between successive testing of 30 minute intervals was not more than 0.001 and 0.1 °C, respectively. After the equilibrium had been reached, the samples were weighed on an analytical balance. To establish the adsorption isotherms, the equilibrium moisture content (EMC) of samples was plotted versus water activity ($a_w$). Moisture adsorption characteristics were evaluated at 25, 35 and 45 °C.

3. Analysis of adsorption data

3.1 Isotherm models

The equilibrium moisture content data were fitted with the six mathematical models presented in Table 1(Sinija and Mishra, 2008). The different models used to fit experimental sorption data were GAB, BET, Oswin, Peleg, Modified Henderson and Modified Halsey equation. The parameters $M_e$, $X_m$, $a_w$ and $t$ in the model represent equilibrium moisture content, monolayer moisture content, water activity and temperature (°C), respectively. Moreover, the other parameters ($A$, $B$, $C$, $K$, $K_1$, $K_2$, $n_1$, $n_2$) are constants of the isotherm.

**Table 1** Different sorption models fitted to the experimental data of Assam green tea powder

| Model | Mathematical expression | Equation No. |
|---|---|---|
| GAB | $M_e = X_m C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$ | (1) |
| BET | $M_e = X_m C a_w / [(1 - a_w)(1 - a_w + C a_w)]$ | (2) |
| Oswin | $M_e = A[\frac{a_w}{1 - a_w}]^B$ | (3) |
| Peleg | $M_e = K_1 a_w^{n1} + K_2 a_w^{n2}$ | (4) |
| Modified Henderson | $M_e = [-\ln(1 - a_w)/(A(t + C))]^{1/B}$ | (5) |
| Modified Halsey | $M_e = [\exp(A + Bt)/\ln(a_w)]^{1/C}$ | (6) |

3.2 Validation of sorption models
In order to calculate the coefficients of various equation models, a nonlinear regression analysis, minimizing the residual sum of squares was applied. The Solver tool, Microsoft Excel 2007 software was used. The predicted data, consisting of equilibrium moisture content at different temperatures and humidity levels, were analyzed for their suitability compared with the experimental data. The main criteria indicated the accuracy of each model were the mean relative error (MRE) and regression coefficient ($R^2$).

3.3 Determination of isosteric heat of sorption
The net isosteric heat of adsorption ($q_{st}$) was calculated from the following form of the Clausius-Clapeyron equation applied at two temperatures:

$$ln\left(\frac{a_{w2}}{a_{w1}}\right) = \frac{q_{st}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ -------------- Equation No. (7)

Where $a_{w1}$ is water activity at temperature $T_1$ and $a_{w2}$ is water activity at temperature $T_2$ and $R$ is the universal gas constant (8.314 J/mol K), the isosteric heat of sorption ($Q_{st}$) was determined by the following equation:

$$Q_{st} = q_{st} + \Delta H_v$$ -------------- Equation No. (8)

Where $\Delta H_v$ is the latent heat of vaporization of pure water at 35 °C (43.53 kJ/mol)

**Results and Discussion**

**Moisture adsorption isotherms of Assam green tea powder**
The experimental results of the equilibrium moisture content at 25, 35 and 45 °C and at six relative humidities are illustrated in Figure 3. At each constant temperature, the equilibrium moisture content (EMC) increases with increasing ERH. In addition, EMC increases with decreasing temperature at constant ERH. The sorption isotherms of Assam green tea powder indicated a slightly decrease in the amount of water activity with an increase in temperature at constant ERH. This characteristic of sorption isotherm was a typical type III sigmoidal curve according to Brunauer's classification. Similar results for the sorption curves have been reported in the literature**.** This type of sorption isotherm is observed frequently in the case of water soluble components present in food (Blahovec and Yanniotis, 2009).

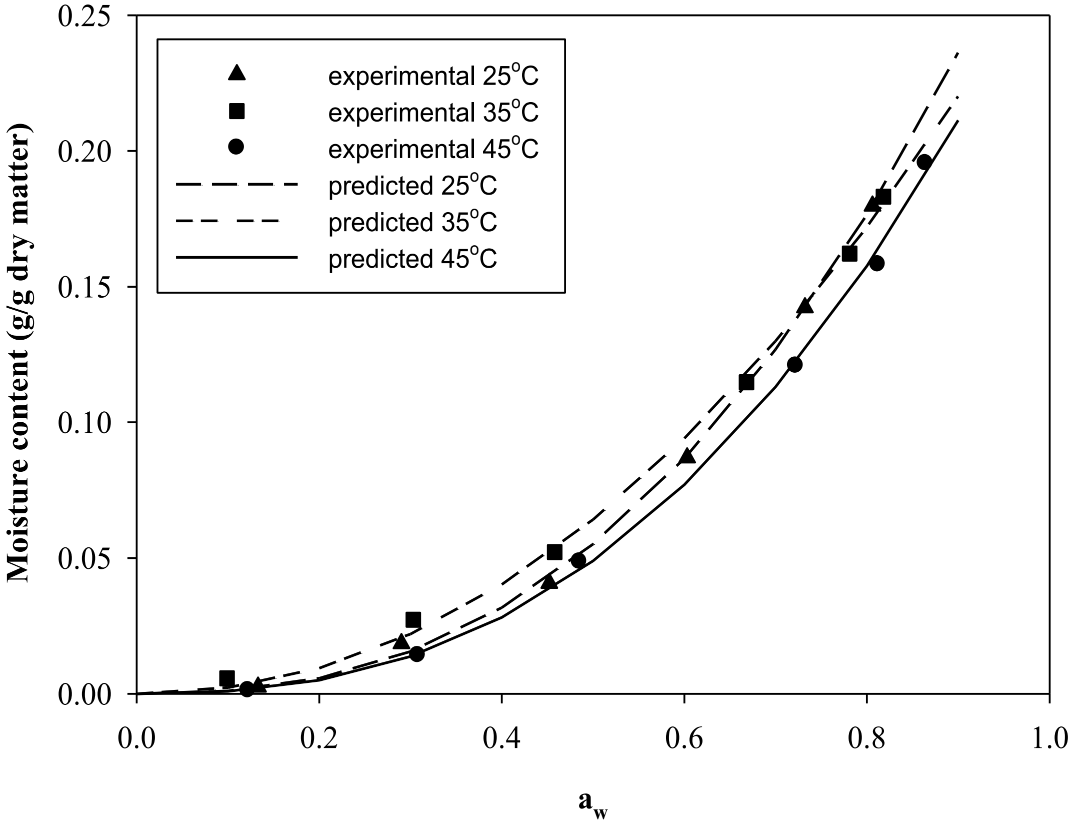


**Figure 3** Experimental and predicted moisture adsorption isotherms of Assam green tea powder using the Peleg equation at different temperatures

**Fitting sorption models to equilibrium moisture data**

The estimated parameters of the different models fitted to the experimental sorption data with regression coefficient ($R^2$) and MRE used in comparing the models are shown in Table 2. From the estimated parameters of different models, it was indicated that the Peleg model (Equation No. 4) gives the best fit to the experimental data for Assam green tea powder with the highest values of $R^2$ and the lowest values of MRE rather than other models for a wide range of water activity. The Peleg model gives MRE values of 7.6816, 14.4841 and 5.0074 with $R^2$ between 0.9980-0.9992. The adsorption curves calculated by the Peleg model are plotted in Figure 3.

**Isosteric heat of sorption**

The study of adsorption isotherms at two different temperatures provides thermodynamic data on isosteric heat of sorption. The net isosteric heat of sorption can be determined from sorption data of the best fitting equation by following the Clasusius-Clapeyron equation (Equation No. 7). In this study, the Peleg model was used to predict the water activity of Assam green tea powder at a given equilibrium moisture content as presented in Table 3. Net isosteric heat of adsorption can be calculated using integration of Clausius-Clapeyron equation as showed in Table 4. The relationships between moisture content and isosteric heats calculated by using the Peleg model at 25 and 45 °C are presented in Figure 4. The isosteric heat of sorption illustrated in Figure 4 was calculated for moisture content ranging from 0.005-0.265 (g/g dry matter). The results indicated that decreasing isosteric heat of sorption with increasing moisture content.

**Table 2** Estimated parameters of the different models fitted to the experimental sorption data for Assam green tea powder

| Model | Constant | Temperature (°C) | | |
|---|---|---|---|---|
| | | 25 | 35 | 45 |
| **GAB** | $X_m$ | 3.0437 | 3.0256 | 3.4338 |
| | $C$ | 0.0249 | 0.0369 | 0.0220 |
| | $K$ | 0.6654 | 0.5782 | 0.6333 |
| | $R^2$ | 0.9963 | 0.9995 | 0.9969 |
| | MRE | 44.2633 | 6.3286 | 82.7192 |
| **BET** | $X_m$ | 0.0417 | 0.0373 | 0.0300 |
| | $C$ | 1.8253 | 3.6479 | 3.5544 |
| | $R^2$ | 0.9813 | 0.9838 | 0.9645 |
| | MRE | 65.8133 | 25.3671 | 150.2282 |
| **Oswin** | $A$ | 0.0555 | 0.0620 | 0.0522 |
| | $B$ | 0.8562 | 0.7425 | 0.7372 |
| | $R^2$ | 0.9858 | 0.9921 | 0.9826 |
| | MRE | 70.2982 | 25.7255 | 161.2924 |
| **Peleg** | $K_1$ | 0.1533 | 0.1372 | 0.1373 |
| | $K_2$ | 0.1533 | 0.1372 | 0.1373 |
| | $n_1$ | 2.4750 | 2.0959 | 2.4882 |
| | $n_2$ | 2.4750 | 2.0959 | 2.4882 |
| | $R^2$ | 0.9992 | 0.9984 | 0.9980 |
| | MRE | 7.6816 | 14.4841 | 5.0074 |
| **Mod. Henderson** | $A$ | 0.2206 | 0.1888 | 0.1484 |
| | $B$ | 0.7203 | 0.8367 | 0.7812 |
| | $C$ | 0.1107 | 1.9679 | 2.4969 |
| | $R^2$ | 0.9957 | 0.9987 | 0.9955 |
| | MRE | 31.0419 | 5.4881 | 72.8108 |

The values of isosteric heat of sorption decreased from 45.6 to 45.2 kJ/mol. The isosteric heats of sorption decreased rapidly with an increase in moisture content until the moisture content reached approximately 0.037 (g/g dry matter) and then it decreased slowly with increasing moisture content as shown in Figure 4. At the point of the equilibrium moisture content which isosteric heat of sorption curve was suddenly changed in slope corresponded well to safe moisture content for the product stability (Vagenus and Marinos-Kouris, 1992). This value of moisture content (0.037 g/g dry matter) is closely to the monolayer moisture content ($X_m$) provided from the equation of BET model (0.030-0.042 g/g dry matter). The monolayer moisture content obtained from the sorption isotherm importance to physical and chemical stability of dried food products (Arslan and Toğrul, 2006). Moreover, the monolayer moisture content is the amount of water needed to form a continuous-adsorbed monolayer over the surface of the foodstuffs and this value is the optimal moisture content for storage of a dried food product (Vagenas and Marinos-Kouris,1992). The monolayer moisture content ($X_m$) obtained from the BET model ranging from 0.030-0.042 (g/g dry matter) as presented in Table 2.

**Table 3** Estimated water activity of Assam green tea powder at a given equilibrium moisture content using the Peleg equation

| Moisture content (g/g dry matter) | $a_w$ at 25 °C | $a_w$ at 45 °C |
|---|---|---|
| 0.005 | 0.190 | 0.200 |
| 0.025 | 0.363 | 0.382 |
| 0.045 | 0.461 | 0.483 |
| 0.065 | 0.534 | 0.560 |
| 0.085 | 0.596 | 0.624 |
| 0.105 | 0.649 | 0.680 |
| 0.125 | 0.696 | 0.729 |
| 0.145 | 0.739 | 0.774 |
| 0.165 | 0.779 | 0.815 |
| 0.185 | 0.815 | 0.853 |
| 0.205 | 0.850 | 0.889 |
| 0.225 | 0.882 | 0.923 |
| 0.245 | 0.913 | 0.955 |

**Table 4** Estimated Net isosteric heat and isosteric heat of adsorption of Assam green tea powder at a given equilibrium moisture content

| Moisture content | Net isosteric heat, $q_s$ (kJ/mol) | Isosteric heat, $Q_s$ (kJ/mol) |
|---|---|---|
| 0.005 | 2.095 | 45.625 |
| 0.025 | 1.959 | 45.489 |
| 0.045 | 1.909 | 45.439 |
| 0.065 | 1.878 | 45.408 |
| 0.085 | 1.855 | 45.385 |
| 0.105 | 1.837 | 45.367 |
| 0.125 | 1.823 | 45.353 |
| 0.145 | 1.810 | 45.340 |
| 0.165 | 1.799 | 45.329 |
| 0.185 | 1.790 | 45.320 |
| 0.205 | 1.781 | 45.311 |
| 0.225 | 1.773 | 45.303 |
| 0.245 | 1.766 | 45.296 |

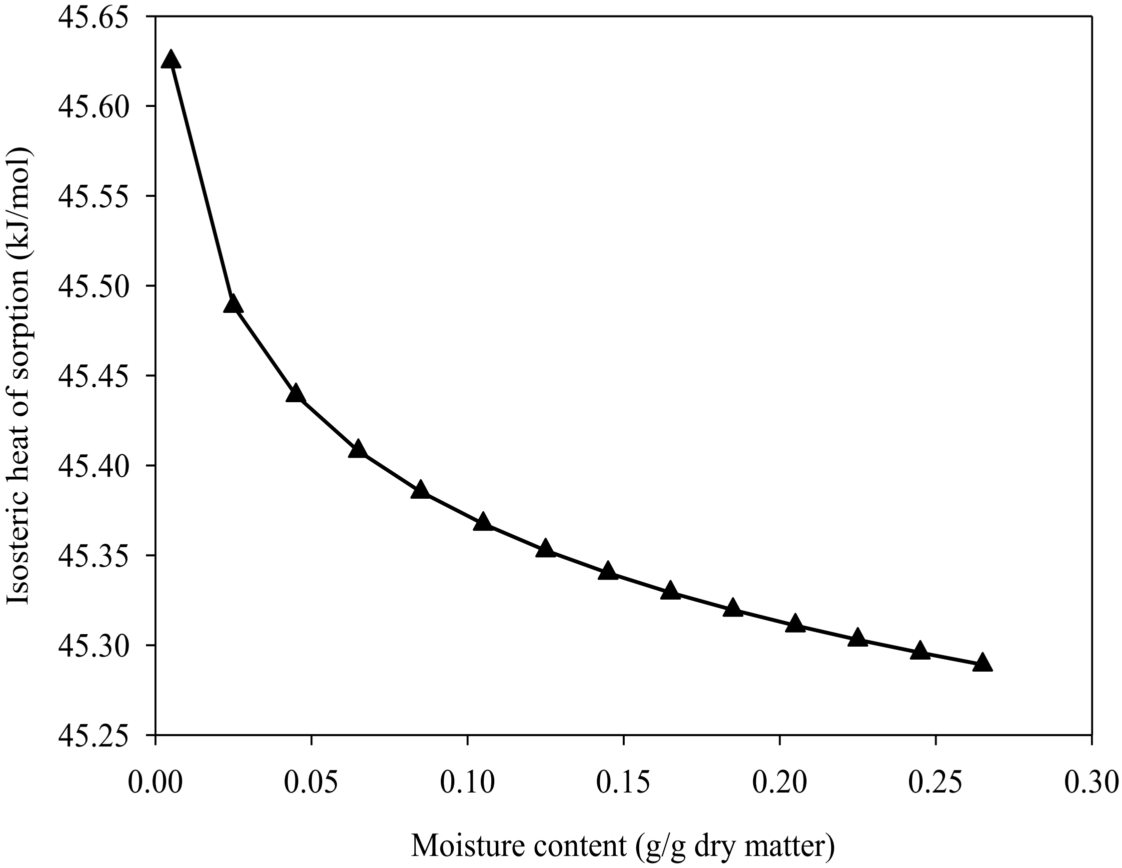


**Figure 4** Variation of isosteric heat for different moisture contents of Assam green tea powder over the temperature range from 25 °C to 45 °C.

## Conclusion

The moisture adsorption isotherms of Assam green tea powder were evaluated at 25, 35 and 45 °C. The powder exhibited typical type III sigmoid curves, according to BET classification and the EMC increased with increasing ERH. Furthermore, EMC increase with decreasing temperature at constant ERH. Among the sorption models chosen, the Peleg equation described the experimental sorption data well over a wide range of temperature and water activity. The isosteric heats of sorption increased with decreasing moisture content and the values ranged from 45.2 to 45.6 kJ/mol. Moreover, the value of equilibrium moisture content at the point when isosteric heat of the sorption curve suddenly changed in slope was at about 0.037 g/g dry matter. This value is close to the monolayer moisture content provided from the BET equation (0.030-0.042 g/g dry matter). It can be concluded from the result that keeping the moisture content of Assam green tea powder below 0.04 g/g dry matter may ensure long shelf life of this product during storage at room temperature.

## Acknowledgements

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