Mathematical modelling of moisture sorption isotherms by using BET and GAB models

S Abdullah¹, S C Keoh², H M Johar³, N A Razak⁴, A R Shaari⁵ and I H Rukunudin⁶
¹,²,⁴,⁵Faculty of Engineering Technology, University Malaysia Perlis, 02100 Padang Besar, Perlis, Malaysia
³,⁶School of Bioprocess Engineering, Schools Complex 3, University Malaysia Perlis 02600 Arau, Perlis, Malaysia

Email: sriyana@unimap.edu.my

Abstract. Fish cracker is a popular local fish based snack in Malaysia. Besides the raw form which can be consumed directly, it is always eaten in the dried form. Thus study of moisture sorption isotherm of fish cracker is essential as to predict appropriate drying and storage conditions consecutively to enhance its nutrients, taste and aroma. In this study, the moisture sorption isotherms of fish crackers from two manufacturers M1 and M2 were developed by using a static gravimetric method at temperatures of 30, 40 and 50°C and water activity (aw) range of 0.04 to 0.80. It is a relationship between equilibrium moisture content (EMC) and aw at a specified temperature. The isotherms exhibited a sigmoid shaped which classified as type II in Brunauer–Emmett–Teller (BET) classification. The increase of temperature decreased the EMC of fish crackers while increase of aw increased the EMC. There was no significant difference of EMC between manufacturers M1 and M2. The moisture sorption isotherms of fish cracker were fitted into predicted isotherms by Guggenheim-Anderson-de Boer (GAB) and BET models. GAB model was found to be the best fit model of fish crackers’ moisture sorption isotherms as compared to BET model.

1. Introduction

There is a lot of local fish based snacks marketed in Malaysia which include dried fish fillet, fish muruku and fish cracker. Fish crackers can be found in Southeast Asia and East Asia regions with Malaysia and Indonesia being the largest producers and consumers [1]. In present study, fish cracker is chosen to be studied since it is the most popular snack which normally being sold in the market in dried form. Nowadays, the growing demand on fish cracker leads to the studies on its shelf life extension and quality enhancement. In Malaysia, they are locally known as ‘keropok’ [2]. Currently, the production of fish crackers is in small scale industries mostly in Johor, Terengganu, Pahang, Kedah and Kelantan [3]. The transition from small scale to large scale production requires scientific knowledge recognition thus premium quality fish crackers could be engineered.

The dried form of fish cracker is usually stored at ambient temperature. However the safe storage moisture content is remain undetermined in consequence, the dried fish crackers are prone to microbial degradation. Moisture is one of the essential parameters that affects the quality of the dried products. Moisture is able to change the product’s mechanical strength by softening and plasticising the starch-protein matrix and thus affecting their texture [4].

¹ To whom any correspondence should be addressed.
Therefore, the knowledge of moisture sorption (adsorption and desorption) behaviour is crucial to ensure the dried products could maintain its quality during storage. Adsorption of moisture occurs when water is adsorbed on the surface of dried fish crackers. In contrast, desorption of moisture occurs when raw fish crackers loss of moisture or when they are dried before delivering to the market. In addition, other factors could also affect the shelf life of fish crackers such as storage conditions and packaging materials. Such storage conditions of temperature and $a_w$ can be gained from the sorption isotherms.

The moisture sorption isotherms of fish crackers can be determined by using a static gravimetric method. This method involves determination of EMC at different temperatures and $a_w$. Several established mathematical models can be used to describe the moisture sorption behaviour of food materials such as Oswin, Peleg, GAB and BET. The BET model is the best known two parameters equation but it is limited to $a_w$ between 0.05-0.45 only [5]. Therefore the three parameters GAB model which is applicable to $a_w$ up to 0.9 is used to compliment the BET model. In comparison to the Oswin and Peleg, the BET and GAB models are able to provide the estimation of monolayer moisture content [6]. Monolayer moisture content ($M_o$) is a critical parameter as it represents the moisture content at which the rate of any associated reaction will be negligible due to the strong binding of water to the surface [7]. In addition, GAB model was reported to be the best fit model over more than 50% of the 163 fruits, meats and vegetables than two parameters models. To date, the data of moisture sorption behavioural studies are limited especially to our local processed food. Therefore in this study, the moisture sorption isotherms of fish cracker from different manufacturers are established. The GAB and BET sorption models are used to perform the mathematical modelling.

2. Materials and Methods

2.1. Materials

Raw and dried fish crackers were purchased from two different manufacturers in Tanjung Dawai, Kedah namely PNK Tanjung Dawai (M1) and Perusahaan Hasil Laut Musliha (M2). Sodium hydroxide, lithium chloride, magnesium chloride, magnesium nitrate, sodium nitrate and potassium bromide were attained from a local chemicals vendors in Kedah, Malaysia.

2.2. Development of sorption isotherms of fish crackers

The sorption isotherms of dried and raw fish crackers were investigated by using a static gravimetric method. The isotherms were developed at temperatures of 30, 40 and 50°C and six $a_w$. Six saturated salt solutions were used where each of them corresponds to $a_w$ and temperature as shown in Table 1. The salt solutions were filled into six different desiccators until one-quarter depth of its bottom part. The desiccators’ containing salt solutions were kept for 24 hours prior experimentation to ensure uniform $a_w$ and temperature.

For adsorption experiment, 2 g of dried fish crackers were weighed and put in petri dishes. The petri dishes were placed in the prepared desiccators and allowed to achieve equilibrium under the controlled conditions. The weight of samples were recorded until constant or the changes of three consecutive readings were less than 0.001 g. The samples were dried in an oven at 105°C for 24 hr to obtain their dry matter weight ($w_{dm}$) [8]. For desorption experiment, the procedure was repeated by using raw fish crackers. Each experiment was performed in triplicate.
Table 1. Water activity values of different salt solutions at different temperature [9].

| Saturated salt solutions | 30°C     | 40°C     | 50°C     |
|--------------------------|----------|----------|----------|
| Sodium hydroxide         | 0.0758   | 0.0626   | 0.0494   |
| Lithium chloride         | 0.1128   | 0.1121   | 0.1110   |
| Magnesium chloride       | 0.3244   | 0.3160   | 0.3054   |
| Magnesium nitrate        | 0.5140   | 0.4842   | 0.4544   |
| Sodium nitrate           | 0.7314   | 0.7100   | 0.6904   |
| Potassium bromide        | 0.8027   | 0.7943   | 0.7902   |

2.3. Mathematical Modelling of Adsorption and Desorption Isotherms
The adsorption and desorption isotherms were constructed by plotting EMC against $a_w$. The EMC was calculated by using equation (1) below:

$$EMC = \frac{w_f - w_{dm}}{w_{dm}}$$  \hspace{1cm} (1)

where $w_f$ is a final sample weight. The EMC from experimentation were compared with EMC predicted by GAB and BET models. The GAB and BET models were showed in equation (2) and (3) respectively.

$$EMC = \frac{M_0 \cdot C \cdot k \cdot a_w}{(1 - k \cdot a_w + C \cdot k \cdot a_w)}$$  \hspace{1cm} (2)

$$EMC = \frac{M_0 \cdot C \cdot a_w}{(1 - a_w)(1 - a_w + C \cdot a_w)}$$  \hspace{1cm} (3)

where, $k$ and $C$ are constants.

For mathematical modelling using GAB model, equation (2) was rearranged to form a polynomial as shown in equation (4) [10]:

$$\frac{a_w}{EMC} = \frac{k^2 - C \cdot k^2}{M_0 \cdot C \cdot k} \cdot a_w^2 + \frac{C \cdot k - 2k}{M_0 \cdot C \cdot k} \cdot a_w + \frac{1}{M_0 \cdot C \cdot k}$$  \hspace{1cm} (4)

and let,

$$\alpha = \frac{k^2 - C \cdot k^2}{M_0 \cdot C \cdot k}, \; \beta = \frac{C \cdot k - 2k}{M_0 \cdot C \cdot k}, \; \varepsilon = \frac{1}{M_0 \cdot C \cdot k}$$

Graph of $a_w/EMC$ against $a_w$ was plotted using Microsoft Excel to find out the values of $\alpha$, $\beta$ and $\varepsilon$. Then $M_0$, $C$ and $k$ were determined using the following relationships:

$$M_0 = \frac{1}{2k \varepsilon + \beta}$$  \hspace{1cm} (5)

$$C = 2 + \frac{\beta}{\varepsilon} \quad \text{and} \quad \beta = \frac{k}{2\varepsilon}$$  \hspace{1cm} (6)

$$k = \frac{f^2 - \beta}{2\varepsilon}$$  \hspace{1cm} (7)

where,

$$f = \beta^2 - 4\alpha \varepsilon$$
For mathematical modelling using BET model, equation (3) was rearranged to a linear form as shown in equation (8) [10]:

$$\frac{a_w}{EMC(1-a_w)} = \frac{C-1}{M_o} \alpha_w + \frac{1}{M_o} C$$  

(8)

The graph of $\frac{a_w}{EMC(1-a_w)}$ against $a_w$, was plotted and the values of $M_o$ and $C$ were obtained from the graph slope and y-intercept respectively. After all parameters in both GAB and BET equations were retrieved, the predicted EMC were calculated by replacing the parameter in the equation.

2.4. Statistical analysis

The best model that fit the experimental EMC was selected based on the highest coefficient of determination ($R^2$) and the lowest mean relative percentage deviation modulus (E) and root mean square error (RMSE). The E and RSME were showed in the equations below [8, 9]:

$$\%E = \frac{100}{N} \sum_{i=1}^{N} \frac{|EMC_{ei} - EMC_{ci}|}{EMC_{ci}}$$

(9)

$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (EMC_{ei} - EMC_{ci})^2 \right]^{1/2}$$

(10)

where EMC$_{ei}$ is a calculated moisture content, EMC$_{ci}$ is an experimental moisture content, $\bar{EMC}_{ei}$ is an average experimental moisture content and N is number of observations.

3. Results and Discussion

3.1. Characteristics of moisture sorption isotherm

Moisture sorption isotherm represents the relationship between EMC and $a_w$ for a food material. The moisture sorption isotherms of fish crackers from M1 and M2 are showed in Figure 1 and 2. As it can be seen from the figures, both desorption and adsorption isotherms of fish cracker exhibited sigmoid shaped curve. Based on BET classification the sigmoid shaped is categorised as Type II isotherm. The type II isotherm occurs due to porosity and unrestricted monolayer-multilayer adsorption of a material which is related to the interaction between adsorbent and adsorbed substances [10]. The type II isotherm was observed on other starch based food materials. For instance, similar observation of moisture sorption isotherms for sweet potatoes has been reported [11]. Another research works also revealed rice cracker [12] and hazelnut cracker [13] exhibited a type II isotherm.

3.2. Effects of temperature and manufacturer on EMC

Result of EMC at each temperature and $a_w$ for manufacturers M1 and M2 are illustrated in Figure 1 and 2. From the graphs, EMC increased as $a_w$ increasing at a temperature for both desorption and adsorption processes. During adsorption process, when the $a_w$ increases more water is available in surrounding air as compared to the dried fish cracker which increases their water vapour pressure difference. Therefore, the tendency of water adsorption process becomes influential. On the other hand, when $a_w$ increased lesser water vapour pressure difference is created between raw fish cracker and surrounding air. At this state less water is desorbed by the surrounding air from the samples.

EMC of fish cracker decreased with an increase of temperature at a specified $a_w$ level which means that fish cracker became less hygroscopic. The increase in temperature causes the decrease in binding energy of water molecules in fish cracker, resulting in the decrease of attractive forces between sorption sites and water molecules [14]. Therefore, the degree of water sorption on fish cracker decreases. Similar trend was also revealed on cassava flour [15] and ginger slides [16].

However by comparing the EMC values between the manufacturers M1 and M2 at all temperatures and RH no significant difference (P>0.05) were observed. This may due to usual recipes in the making
of fish cracker that were used by both manufacturers. In addition, the EMC for desorption of fish cracker was higher than that of adsorption isotherm, resulting in hysteresis phenomenon which is the difference between adsorption and desorption isotherms. This phenomenon was occurred due to the difference when emptying and filling of moisture in the pores of fish cracker for desorption and adsorption respectively [17]. It may also due to the pre-drying samples used for adsorption. The pre-drying process modified and deactivated by physical (closing pores by shrinkage) and/or chemical processes the binding sites present in the leaves. The structural changes of pores and surface characteristic modifications could reduce the ability of moisture pick up by the samples during adsorption [18].

![Graph](image1.png)

**Figure 1.** Moisture desorption isotherms of fish crackers.
3.3. Mathematical modelling of moisture sorption isotherms

The experimental EMC of fish crackers were compared with predicted EMC by GAB and BET models. Table 2 shows the comparison results from evaluation of statistical parameters. For M1 fish cracker, the predicted EMC for dried samples at 30°C by GAB model was found as the best fit model. This was due to the highest $R^2$ (0.9987), and the lowest E (3.57) and RMSE (0.0028) as shown in Table 2. Similarly, GAB model was also found to fit desorption process of M2 raw fish cracker at 30 and 40°C well.

In general, for both of the adsorption and desorption of fish cracker, GAB model prediction showed closer to experimental EMC than BET did. Therefore, GAB model is the most suitable model for the description of experimental sorption data of the fish crackers. This finding was comparable with others. For instance, sorption isotherms of cassava [19], chili pepper [20] and rice cracker [12] can be described well by using GAB model. In addition, European Project Group COST 90 had recommended GAB equation in the characterization of sorption behaviour of food products [21, 22].

| Manufacturer | Sorption Isotherm | Model | Statistical Parameter | Temperature (˚C) |
|--------------|-------------------|-------|-----------------------|-----------------|
|              |                   |       | $R^2$                 | 30  | 40  | 50  |
| M1 Desorption| GAB               | $E$ (%)| 3.57                  | 5.68 | 10.50 |
|              | RMSE              |       | 0.0028                | 0.0028 | 0.0042 |
|              | $R^2$             |       | 0.9446                | 0.9398 | 0.9357 |
|              | BET               | $E$ (%)| 18.07                 | 17.32 | 23.57 |
|              | RMSE              |       | 0.0578                | 0.0423 | 0.0464 |
|              | $R^2$             |       | 0.9979                | 0.9982 | 0.9922 |
| M1 Adsorption| GAB               | $E$ (%)| 2.03                  | 3.80  | 7.46  |
|              | RMSE              |       | 0.0033                | 0.0027 | 0.0049 |
|              | $R^2$             |       | 0.9163                | 0.9158 | 0.9185 |
|              | BET               | $E$ (%)| 15.37                 | 17.48  | 21.13 |
|              | RMSE              |       | 0.0564                | 0.0533 | 0.0488 |
|              | $R^2$             |       | 0.9982                | 0.9979 | 0.9969 |
| M2 Desorption| GAB               | $E$ (%)| 5.02                  | 7.00   | 8.17   |
|              | RMSE              |       | 0.0032                | 0.0030 | 0.0034 |
|              | $R^2$             |       | 0.9257                | 0.9486 | 0.9335 |
| M2 Adsorption| GAB               | $E$ (%)| 23.33                 | 19.70  | 22.30  |
|              | RMSE              |       | 0.0691                | 0.0443 | 0.0488 |

In contrast, BET model has showed a fair fitting to the experimental EMC up to $a_w$ of 0.6. This
occurrence has proven limitation of BET model on certain \( a_n \) range [19, 23]. Similar result was also observed on rice cracker [12], pistachio nuts shell, \( M. \ esculenta \) mushrooms and spray dried tomato pulp [24].

4. Conclusion

The establishment of moisture sorption isotherms of fish cracker is essential in providing information for the storage and drying of fish crackers. The EMC established over desorption process could aid setting up drying process properly. In addition, EMC determined during the adsorption process could promote appropriate storage procedures. The sorption isotherms of fish cracker exhibited type II isotherm according to BET classification. At constant \( a_n \), the increase in temperature caused the decrease in EMC. When \( a_n \) increased, the equilibrium moisture content of fish cracker increased at constant temperature. The desorption isotherm was higher than adsorption isotherm, resulting in hysteresis phenomenon. All of moisture sorption isotherms of fish crackers form different manufacturers did not show a significant difference. GAB model has showed the best fit to experimental EMC for desorption process at 30°C. Therefore GAB model was the most suitable model in describing the experimental sorption data of fish cracker. A further research on the effects of drying, storage and packaging material on final product quality of fish crackers could be carried out in order to extent the shelf life.

References

[1] Zulkarnain O W, Zunaidi I, Tarmizi I M, Luqman M, Kharudin A and Redhwan A M 2014 Aust J Basic Appl Sci 8 450–454.
[2] Huda N, Li Leng A and Xian Yee C 2010 Asian J Food Agro-Industry 3 473–482.
[3] Dibar Shah S S 2013 Improvement of Drying Process in Fish Cracker Production Thesis Universiti Malaysia Pahang.
[4] Sacchetti G, Pittia P and Pinnavaia G G 2005 Int J Food Sci Technol 40 655–663.
[5] Al Muhtaseb A H, McMinn W A and Magee T R A 2002 Trans IChemE Part C 80 118–128.
[6] Yanniotis S and Blahovec J 2009 LWT - Food Sci Technol 42 1688–1695.
[7] Pratheeba Yogendarajah, Simbarash Samapundo, Frank Devlieghere and Sarah De Saeger B D 2015 LWT - Food Sci Technol 64 177–188.
[8] International A. Official methods of analysis of AOAC International 1997 16th ed. 35 Choice Reviews Online 35-0912.
[9] Greenspan L 1977 J Res Natl Bur Stand 81 89–96.
[10] Akoy E Von Horsten D and Ismail M 2013 Int Food Res J 20 883–890.
[11] Aktas T, Ulger P, Daglioglu F and Sahin F H 2014 Bulg J Agric Sci 20 512–522.
[12] Siripatrawan U and Jantawat P 2006 Food Sci Technol Int 12 459–465.
[13] Skibsted L H, Risbo J, Andersen M L B T-C D and Pie F of F and B 2010 Woodhead Publishing Series in Food Science, Technology and Nutrition 21–28.
[14] Oh S, Lee E J and Hong G P 2018 LWT - Food Sci Technol 94 73–78.
[15] Kurtis L. D 2014 Size Airtight Plastic Containers using the Guggenheim-Anderson-de Boer (GAB) Model.
[16] Ananthreddigari A R 2014 Determination of sorption isotherm and shelf life study of hazelnut cracker using GAB model Thesis University of Wisconsin-Stout.
[17] Miranda M, Vega-Galvez A, Sanders M, Lopez J, Lemus-Mondaca R and Martinez E 2012 J Food Bioprocess Technol 5 1686–1693.
[18] Moreira R, Chenlo F, Vazquez MJ, Camean P 2005 J Food Eng 71 193–199.
[19] Ayala-Aponte A A 2016 Thermodynamic properties of moisture sorption in cassava flour DYN 83 139–145.
[20] Seid R M and Hensel O 2012 Agric Eng Int CIGR J 14 163–172
[21] Suzanne Nielsen 2004 Handbook of Food Analysis, Physical Characterization and Nutrient Analysis 2nd Ed Marcel Dekker Inc 270 Madison Ave New York 2164
[22] Koua B K, Koffi P M E, Gbaha P and Toure S 2014 J Food Sci Technol 51 1711–1723
[23] José Edgar Zapata M, Oscar Albeiro Quintero C and Luis Danilo Porras B 2014 Agron Colomb 32 52–58
[24] Timmermann EO, Chirife J, Iglesias HA 2001 J Food Eng 48 19–31

Acknowledgement
This research work is supported by Ministry of Education Malaysia under Fundamental Research Grant Scheme (FRGS) (Grant no.: FRGS/1/2018/TK02/UNIMAP/03/3) and University Malaysia Perlis, Malaysia.