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Analysis of the Moisture Sorption Isothermic Characteristics of Dried Salted *Glossogobius Giuris*

Rea Joan M. Atienza*, Aprilyn E. Calvario, Leny V. Salmingo

Polytechnic University of the Philippines – Santa Rosa, Tagapo, Santa Rosa Laguna 4026, Philippines
rjmatienza@pup.edu.ph

Glossogobius giuris, commonly known as white goby or biyang puti, is a local fish species in Laguna de Bay, Philippines, commonly sun-dried for selling. Traditional sun-drying of salted white goby has been a prevailing practice, but no initiatives were accounted to study in detail and improve its drying, storing, and packaging process. This study then identifies the water activity (a_w) and equilibrium moisture content (EMC) of dried white goby using different salt proportions, storage temperatures, and packaging mechanisms which were used to model its moisture sorption isotherm. Modelling its moisture sorption isotherm will aid in designing and optimizing the drying process, storage techniques, and packaging mechanism. Modelling techniques, like Oswin, Smith, Halsey, and Henderson models, as well as Langmuir, Brunauer-Emmett-Teller (BET), and Guggenheim-Anderson-de Boer (GAB) equations, were considered and analyzed to characterize the moisture sorption isotherm of these dried salted white goby. The best fit among these models was tested using root mean square error (RMSE), mean relative percentage difference (RPD), and coefficient of determination (R^2). Analysis was done at temperatures of 15 °C, 25 °C, 35 °C and 40 °C that correspond to water activity (a_w) ranging from 0.10 to 0.80, which varied by different salt saturation, with and without packaging conditions. Among the models utilized and tested, the GAB model best projected the EMC of the salted white goby both with and without packaging with the highest R^2 greater than 0.94 and lowest RMSE of less than 0.020, which will lead to the detail description of moisture sorption characteristics of dried salted goby necessary for the improvement of the drying process. T-tests for independent samples were also employed and found that statistically, there was no significant difference between the a_w and EMC with a p-value of 0.96 and 0.91 for dried goby with and without packaging, suggesting further improvement can be made upon the packaging mechanism to increase its efficacy.

1. Introduction

The White Goby, scientifically known as *Glossogobius giuris*, is a small freshwater fish commonly found in rivers, streams, and brackish water areas across the Philippines. It has a distinct white coloration with dark markings, making it easily identifiable. Fishing this white goby has been an established industry in Rizal and Laguna province, specifically those alongside Laguna de Bay, where bigger catches are sold fresh to nearby markets while smaller ones are sun-dried before selling. Although the supply from the Bay is abundant from May to August and less from October to December (Lagbas et al.,2017), locals have found ways to reach other provinces like Bataan and Bulacan to run the industry for the whole year. While bigger ones are directly sold fresh to markets by more prominent business owners, locals are more involved in sun-drying the smaller ones before selling, providing local communities with nourishment and income for generations. Although traditional sun-drying has long been a tradition and industry, initiatives still need to be accounted for to scientifically study in detail and further improve its drying, storing, and packaging process.

One crucial attribute of any dried product that influences the drying process's efficacy and shelf life is the moisture sorption characteristics of the product. Moisture sorption characteristics describe how the moisture content in food products is related to its water activity, usually represented by sorption isotherm shown via graphical and mathematical modelling. It is crucial in designing and maximizing technological food processes that require predicting food stability and shelf life, such as drying, handling, packaging, and storing (Aviara,

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2020). Though there are plenty of studies about moisture sorption isotherm characteristics and modelling of dried fish as suggested by the included references, none is about white goby. Packaging studies are also available, such as the study of Mohammed et al. (2024) on standard low-density polyethylene (LDPE) plastics but no one has studied its usage on storing dried fish in the Philippines, mainly of white goby. This study is then about evaluating the water activity, equilibrium moisture content across different temperatures, and salt proportions with or without LDPE plastic packaging as well as modelling the moisture sorption isotherm specifically of white goby, to aid in optimizing its drying process, storage techniques, and designing packaging mechanism of the dried fish.

2. Materials and Methods

2.1 Materials

White goby samples were bought fresh from the locals, iced, and chilled using a polyethylene container. Then they were split open and cleaned thoroughly, removing the gills and all the internal parts, producing a total of 3.2 kg split white goby, which were then grouped into 400 g each. To prepare them for drying, each 400 g was sprinkled and mixed evenly with 5 %, 8 %, 10 %, or 15 % table salt proportions necessary to achieve four water activities within the targeted range. These were then sundried for about 5 to 7 h. This produced eight sets of 400 g each of salted dried gobies, half of which were ordinarily packed using standard (LDPE) plastics with dimensions 20 cm by 20 cm sealed using a heat source, and the rest were left unpacked. Both packed and unpacked were further divided into 100 g each, assigned and exposed to either 15 °C, 25 °C, 35 °C, or 40 °C temperatures and were left until equilibrium. These temperatures were controlled using a do-it-yourself insulated material placed in designated areas to meet the temperature requirements. In summary, 32 sets of 100 g each were prepared, 16 of which were packed and 16 unpacked, each with assigned storage temperatures and salt proportions.

2.2 Methods of Developing the Moisture Sorption Isotherm

When equilibrium was reached, water activity (a_w) was identified using a water activity meter. Water activity is the product's water vapor pressure ratio to pure water pressure given the same conditions. Thirty-two water activities were identified for each 100 g sample, 16 of which were from packed and 16 from the unpacked gobies, each with different temperatures provided above. These water activities per temperature per type of packaging were correlated to the quantity of water on the dried product, known as Equilibrium Moisture Content (EMC), to evaluate the moisture sorption isotherm of the dried fish. EMC of a product is the moisture level at which it is already in equilibrium with the surrounding relative humidity and temperature, so it no longer loses or gains moisture. EMC was quantified using the ratio of the goby's difference in mass before and after drying and storing to its initial mass, as shown in the following equation.

$$EMC_{exp} = \frac{w_f - w_i}{w_i} \quad (1)$$

This EMC was then compared with the most common theoretical sorption isotherm models (Majd et al., 2022). These were described by Oswin in Eq(2), Smith in Eq(3), Halsey in Eq(4), Henderson in Eq(5) as well as Langmuir in Eq(6), Brunauer-Emmett-Teller (BET) in Eq(7), and Guggenheim-Anderson-de Boer (GAB) in Eq(8) equations as shown:

$$EMC = C\left(\frac{a_w}{1-a_w}\right)^n \quad (2)$$

$$EMC = C_1 + C_2 ln(1-a_w) \quad (3)$$

$$EMC = \left(-\frac{C}{ln a_w}\right)^{1/n} \quad (4)$$

$$EMC = \left(-\frac{\ln(1-a_w)}{C}\right)^{1/n} \quad (5)$$

$$\frac{1}{CM_o} = a_w\left(\frac{1}{M_w} - \frac{1}{M_o}\right) \quad (6)$$

$$EMC = \frac{M_0 C a_w}{(1-a_w) + (C-1)(1-a_w)a_w} \quad (7)$$

$$EMC = \frac{M_0 C k a_w}{(1-ka_w) + (1-ka_w+cka_w)} \quad (8)$$

Where k, n, Mo, and C are all constants, Mo represents the monolayer moisture content, and C is the constant related to the net heat of sorption energy. Using mathematical manipulations and Microsoft Excel, these constants were identified and used to calculate each EMC associated with a_w, represented as EMC theoretical (EMC_{theo}). The best fit among EMC_{theo} was obtained using the mentioned models, and EMC_{exp} from experimental data was tested using mean RPD, RMSE, and direct non-linear regression analysis through R^2.

3. Results and Discussions

The four different salt saturations provided upon drying white goby, the packaging used, and the other temperature exposure influenced a_w and experimental Equilibrium Moisture Contents (EMC_{exp}) as shown in Figure 1. Careful analysis, observations, and computations were employed to model these quantities and yield the following results.

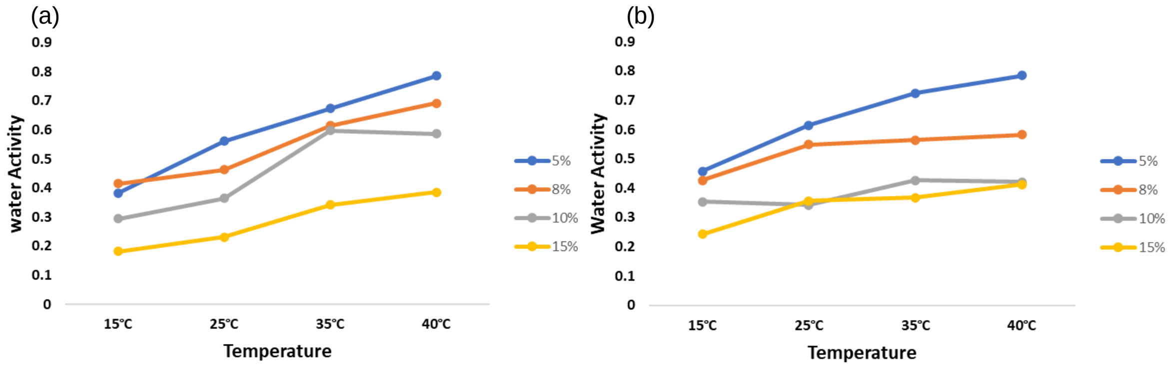

Figure 1: Water Activity (aw) of dried goby (a) with plastic packaging (b) without packaging in different salt proportions across different temperatures.

Across different salt saturations, water activity (a_w) increases with temperature, probably because of an increasing amount of surrounding water vapor (Correa et al., 2015). The most minor water activities were identified under the highest salt proportion of 15 %. Also, for salted dried goby packed using standard LDPE plastics, there is the smallest increase in the a_w of salt-to-goby proportions of 15 % and a drop in a_w for 10 % at 40 °C. The salt proportion has increased considerably for dried goby without packaging, only at 5 %. The rest has a minimal increase or even a drop in a_w. These results imply that generally, high salt proportions have lesser water activity and a lesser chance of it increasing across increasing temperatures. Hence, a higher salt-to-goby proportion is suggested. Higher salt proportion is also beneficial since a_w does not increase much with temperature so that it can be stored even at room temperature or even higher.

Furthermore, packed dried goby have more predictable water activity since they are not exposed to outside atmospheric conditions. Therefore, regulating and reducing it is much easier than white goby without packaging. Reducing the water activity helps prolong the shelf life of a product since it lessens the chance of microbial growth and spoilage, as Rifna et al. (2022) mentioned. Hence, an effective packaging material is recommended. In addition, when a_w of salted dried goby in packaging was statistically compared with no packaging, a p-value of 0.96 was obtained. This computed p-value is much greater than the 0.05 level of significance, implying no significant difference between the a_w values. Though this is the case, it is still advisable to use packaging to protect the product from other contaminants. Improving the packaging mechanism to have statistically significant results is just suggested.

Across different salt saturations, the smallest EMCs were identified under the highest salt proportion of 15%, indicating that the dried goby has more moisture stability in higher salt concentrations. Also, for salted dried goby packed using standard LDPE plastics, the EMC increases with temperature agrees with the findings of Echavarria et al. (2021) in their study of the sorption isotherm of dry silage of red tilapia viscera. As they have mentioned, the increase in EMC may be attributed to the complex interaction between the food profiles and surrounding water vapor content that changes according to varying temperatures and a_w. This also agrees with the result of Ikrang and Umani (2019), who stated that there is a linear positive relationship between the moisture level in the dried catfish and temperature. Predictably, since dried goby has low starch content, these results of EMC vs. temperature contradicts the results of Arslan-Tontul (2020), which showed that EMC of high-starched food decreases with temperature. Further differences with the general trends of EMC in temperature may be due to drying mechanisms such as solar drying, varying time exposures, and storage techniques.

Almost the same results were obtained for the EMC of salted dried goby without packaging, as shown in Figure 2. However, some were dropped in EMC at 35 °C for salt saturation with proportions of 8 % and 15 %. The EMC was also closer to each other than those with packaging. These may be attributed to the fact that water vapor permeability was not controlled. This implies EMC regulation is more accessible with packaging since results are more consistent. This is crucial in extending the product's shelf life as regulating EMC prevents mold and bacteria growth, minimizing microbial degradation. Packaging techniques for dried fish, such as using LDPE, are known to extend storage stability, as supported by the study of Otolowo (2019).

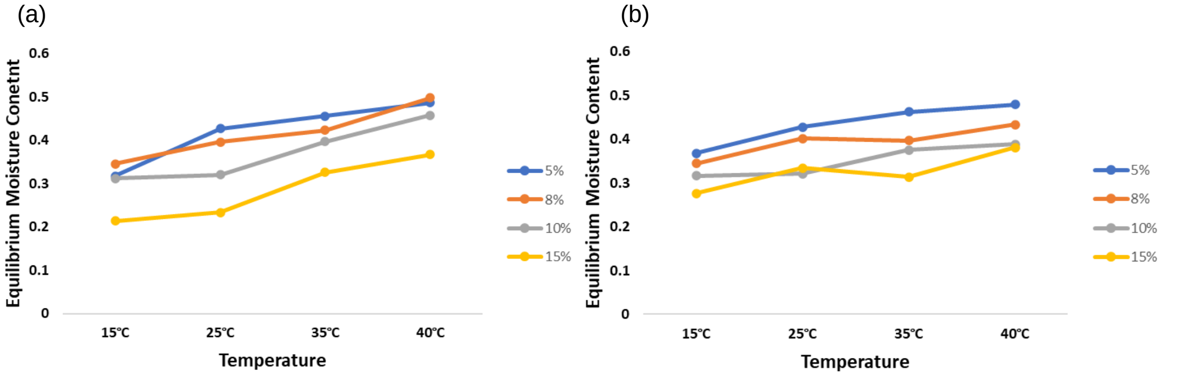

Figure 2: Moisture Content (EMC) of dried goby (a) with plastic packaging (b) without packaging in different salt proportions across different temperatures.

Furthermore, using a t-test for independent samples, EMC with and without packaging were statistically compared, and a p-value of 0.91 was obtained, which is much greater than the 0.05 level of significance level. This implies that EMC obtained when there was packaging is no different from when there was none. However, it is still advisable to have a packaging mechanism since, as shown by the graphs, EMCs with packaging are more predictable, providing a reliable shelf life. Further improvement can be made on plastic packaging, such as vacuum sealing them to result in a statistically significant difference.

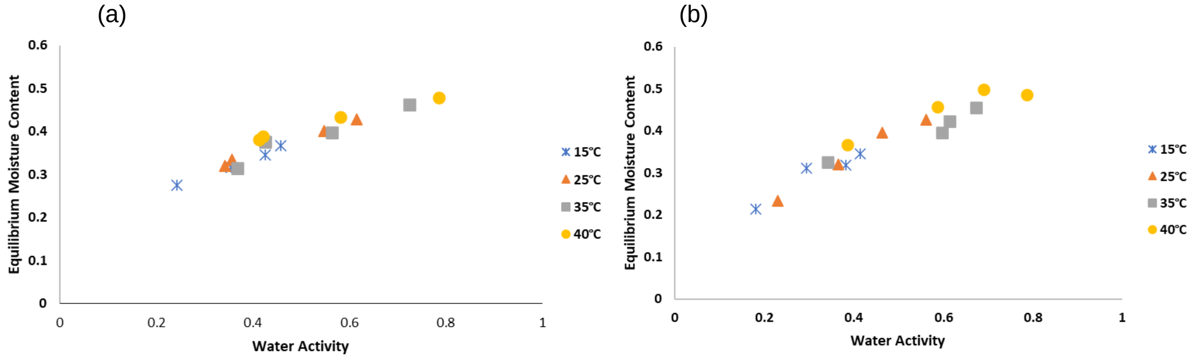

Figure 3: Equilibrium Moisture Content (EMC) of dried goby vs. Water Activity (a)with plastic packaging (b) without packaging in different salt proportions across different temperatures.

The association between the EMC and a_w is scientifically known as moisture sorption isotherm. Moisture sorption isotherm provides valuable information about product stability. Studying and modelling it help develop, improve, and optimize the drying, packaging and storing processes. Figure 3 above represents the moisture sorption isotherm curves of the dried goby with and without LDPE packaging. As shown in the figure, for the identified temperatures, EMC increases with a_w consistent with the findings of Ruan et al. (2022) in their study of microwave-dried tilapia fillets. As they pointed out, water adsorption increases the product's moisture content as water activity increases. It is also consistent with the study of Echavarria et al. (2021) when they modelled the moisture sorption isotherm of red tilapia. The results also agree with the ideal storage temperature of 15-25 °C having the smallest EMC vs. a_w, as Gichau et al. (2019) mentioned that the moisture content for maximum product stability falls with a_w values between 0.2 to 0.3. Since not much difference was identified in the moisture sorption isotherm of the dried goby with and without packaging, improvement in packaging is highly recommended.
These results were then compared, as shown in Table 1, with existing moisture sorption isotherm models such as Oswin, Smith, Halsey, Henderson, Langmuir, BET, and GAB equations to verify that these experimental data were also statistically fitted across established models.

Table 1: Best Fitting of Experimental Equilibrium Moisture Content (EMC_{exp}) to the Different Established Moisture Sorption Isotherm Models

Moisture Sorption Isotherm Models	With packaging			Without packaging		
	RMSE	R^2	RPD (%)	RMSE	R^2	RPD (%)
BET	0.0171	0.9031	0.2483	0.0356	0.2165	4.1379
GAB	0.0195	0.9438	0.6723	0.0143	0.9331	0.1468
Oswin	0.0289	0.8825	0.1313	0.0186	0.8898	0.0844
Smith	0.0234	0.5121	0.0100	0.0103	0.8802	0.0100
Halsey	0.0343	0.8368	0.0959	0.0211	0.8579	0.1115
Henderson	0.0240	0.9165	0.2136	0.0161	0.9157	0.0693
Langmuir	0.0195	0.9430	0.2469	0.0145	0.9312	0.1340

Considering salted dried gobi with packaging, the lowest RMSE was identified using the BET model. However, BET was correlated using a_w less than 0.5, making the results inconclusive for the rest of a_w. The GAB and Langmuir isotherm models are followed on the list. The GAB model obtained the highest R^2 of 0.9438, implying the presence of the strongest correlation. As for the RPD, the Smith model had the lowest, but it only had a moderate correlation. Comparing experimental data with the mentioned moisture sorption isotherm models, GAB was the best fit with the second lowest RMSE of 0.0195, considerable RPD of 0.6723 %, and the highest R^2 of 0.9438.

Furthermore, for salted dried gobi without packaging, the lowest RMSE and RPD of 0.0103 and 0.0100 were identified using the Smith model. However, Smith was correlated using a_w greater than 0.5, making the results inconclusive for the rest of the experimental data. Followed on the list is GAB with RSME of 0.0143, also having the highest R^2 of 0.9331, implying the presence of the strongest correlation. Comparing experimental data with the mentioned moisture sorption isotherm models, GAB was best fitted with the second lowest RMSE of 0.0143, considerable RPD of 0.1468 %, and the highest R^2 of 0.9331.

Among the mentioned models, dried goby both with and without packaging were mostly correlated to GAB model. This agrees with the results of the study of Ikrang et al. (2023) about tilapia fish and Rahman et al. (2019) in their study of dried tuna fish.

Identifying the best-fit model for a product is essential in designing and optimizing the drying, packaging, and storing conditions and techniques since they provide information regarding the product's storage stability and shelf life. Considering that the salted dried goby with and without LDPE packaging have strong correlations with the GAB model, future researchers can look into this model to predict and study the water activity and equilibrium moisture content at any given drying or storage temperature of the dried fish, allowing them to improve its drying, packaging and storing mechanism.

4. Conclusions

The smallest a_w and EMC were recorded in the highest salt proportion, implying more excellent moisture stability and, thus, the longer shelf life of white goby in higher salt content. The a_w and EMC were also found to increase with temperature for dried goby with and without LDPE packaging. When the a_w of salted dried goby in packaging was statistically compared with no packaging using the t-test for independent samples, the p-value implied no significant difference between them. The same conclusion was gained for EMC. These data suggested that further improvement can be made in the packaging mechanism of the dried white goby to obtain statistically significant results. The moisture sorption isotherm generated showed that at a constant temperature, EMC increases with a_w, which is consistent with related literature. The smallest EMC vs. a_w was also recorded at 15-25 °C, suggesting it to be the recommended storage temperature. Through mathematical manipulations and Microsoft Excel, EMC from the experiments were compared to the EMC from Oswin, Smith, Halsey, Henderson, Langmuir, Brunauer-Emmett-Teller (BET), and Guggenheim-Anderson-de Boer (GAB) models. The best fit among these models was computed using RPD, RMSE, and R^2. The GAB model was the best fit with the highest R^2 for both with and without LDPE packaging. These combined results can be used to improve the drying process of white goby with regards to salt proportion, storage temperatures and packaging materials for better efficacy.

Nomenclature

a_w – water activity
BET – Brunauer-Emmett-Teller
C, C1, C2 – energy constant
EMC– equilibrium moisture content, %
EMC_{exp}, EMC_{theo} .– experimental and theoretical equilibrium moisture content, %

GAB– Guggenheim-Anderson-de Boer
LDPE – low-density polyethylene
Mo - monolayer moisture content
R^2 – coefficient of determination
RMSE – root mean square error
RPD– relative percentage difference, %
w_f, w_i- final and initial mass

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