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Freeze-drying of squid: a study to investigate the effect of different pre-treatments

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Among food preservation methods, freeze-drying is the method that preserves nutritional and sensory qualities the most. This study investigated the freeze-drying kinetics of differently pretreated squid samples and their compatibility with mathematical models. Fresh squid samples were sliced into strips, subjected to eight pretreatments including blanching, blanching with salt, and osmotic dehydration at different salt concentrations, and then freeze-dried. Drying times were between 420 - 600 min and pretreatments were found to be effective in decreasing drying time and final moisture content. Effective moisture diffusivity values were calculated between 4.74×10^{-10} - 2.41×10^{-10}. In the compatibility tests of the drying data with the mathematical models, the control samples had an R^2 value of 0.999997 with Two-term, while all pretreated samples fit the Alibas model with R^2 values higher than 0.99999.

Keywords: Blanching; Freeze-drying; Mathematical modeling; Osmotic dehydration; Squid

INTRODUCTION

Freeze-drying, or lyophilization, is widely acknowledged as a superior method for preserving heat-sensitive food items. It operates at low temperatures, which helps in retaining the nutritional quality of moisture-rich foods like seafood. This method prevents the thermal degradation of sensitive nutrients, ensuring that seafood maintains its original nutritional profile. Freeze-drying causes less lipid oxidation compared to traditional drying methods like hot-air drying. This is crucial for seafood, which is rich in unsaturated fatty acids that are prone to oxidation. Lower lipid oxidation helps in maintaining the quality and extending the shelf life of seafood products [1, 2]. It also helps in preserving the sensory properties of color, texture, and flavor. This is particularly important for consumer acceptance and marketability [1-3].

Despite its benefits, the industrial application of freeze-drying in seafood processing is not widespread. This is due to the high costs and the need for specialized equipment. Various pretreatment methods have been explored to enhance the efficiency and quality of freeze-dried products. Blanching and osmotic dehydration (OD) are effective pretreatment methods that can significantly enhance the freeze-drying process [4, 5]. Blanching can reduce the drying time and energy consumption during freeze-drying. Also, it helps in retaining the physical and sensory qualities of the dried product, such as color, texture, and rehydration properties [6]. OD reduces the initial water content of the food, which shortens the subsequent freeze-drying time and improves energy efficiency. OD helps in maintaining the nutritional and sensory quality of the freeze-dried product [7, 8].

In the literature, there are freeze-drying studies of seafood such as shrimp, scallops, mussels, squid, shrimp, salmon [9-12]. However, very few of these studies examine the effect of pretreatment procedures before freeze-drying on the drying process. Squid is rich in essential nutrients, including high-quality protein, long-chain omega-3 fatty acids (DHA and EPA), vitamins (E, B12), and minerals (Na, K, Mg, P, Cu, Zn). Despite its low fat content, squid offers a favorable omega-3/omega-6 ratio, which is beneficial for heart health [13, 14]. This study aims to evaluate the drying characteristics of squid subjected to blanching, blanching in saltwater, and osmotic dehydration pretreatments and to determine the most suitable mathematical models for characterizing the freeze-drying behavior of both untreated and treated samples.

MATERIALS AND METHODS

Sample preparation

Squid was brought from a local fish market in Istanbul/Türkiye and stored at +4 ± 2 °C in a refrigerator (model 1050T; Arçelik, Eskişehir, Türkiye). For each experimental step, squid samples were sliced into 5.0 ± 0.15 g strips. Weights were

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recorded using a digital balance (AS 220.R2, Radwag, Radom, Poland). Initial moisture content was determined in accordance with AOAC (2005) guidelines [15] by drying the samples for 4 h at 105 °C in a KH-45 hot air oven (Kenton, Guangzhou, China).

Drying experiments

Nine groups of squid samples (each 5.0 ± 0.15 g) were prepared under different pretreatment conditions. For blanching, samples were immersed in 100 mL of deionized water at 90 °C for 1 min (B – 1 min) or 5 min (B – 5 min). In the saltwater blanching treatment, squid were blanched in 10% (w/v) salt solutions at 90 °C for 1 min (B 10% – 1 min) and 5 min (B 10% – 5 min). Osmotic dehydration (OD) treatments involved immersing the samples in 10% and 20% (w/v) salt solutions at room temperature for 5 and 10 min each (OD 10% – 5 min, OD 10% – 10 min, OD 20% – 5 min, OD 20% – 10 min).

After pretreatments, excess surface moisture was removed, and samples were immediately transferred to a freeze dryer (Labart LFD-10N, ART Laborteknik, Istanbul, Türkiye). During the drying cycle, the vacuum was released every 60 min to allow samples to be weighed and photographed within 2 min, after which drying resumed. The process continued until the moisture content dropped below 5% of the dry matter, after which the samples were vacuum-sealed.

Mathematical modeling

Moisture transport during drying was evaluated using Fick's Second Law, which provides a theoretical basis for modeling diffusion-driven moisture migration. During the constant rate period, moisture removal primarily occurs from the surface; in the falling rate period, internal diffusion dominates [16, 17]. The moisture content (M, kg water/kg dry matter) and the dimensionless moisture ratio (MR) were calculated as in Eq. 1 [16].

$$M = \frac{m_w}{m_d} \quad (1)$$

where m_w denotes the water content (kg), and m_d denotes the dry matter content (kg). M_t is the moisture content at any moment, M_e is the equilibrium moisture content, M_0 is the initial moisture content (kg water/kg dry matter), and MR is the moisture ratio (dimensionless) [18]:

$$MR = \frac{M_t - M_e}{M_0 - M_e} \quad (2)$$

Drying data were analyzed using Statistica 8.0 (StatSoft, Tulsa, USA). The suitability of each model was initially assessed based on regression analysis. The coefficient of determination (R^2) was used to evaluate the model's accuracy, with values close to 1 indicating high correlation [18] (Eq. 3). Additional indicators such as chi-square (χ^2) and root mean square error (RMSE) were also used to evaluate model performance, with values closer to zero indicating better fit [19] (Eqs. 4, 5):

$$R^2 \equiv 1 - \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{\sum_{i=1}^{N}\left(MR_{exp,i} - \left(\frac{1}{n}\right)\sum_{i=1}^{N} MR_{exp,i}\right)} \quad (3)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N - z} \quad (4)$$

$$RMSE = \left(\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2\right)^{\frac{1}{2}} \quad (5)$$

where MR_{exp} and MR_{pre}, define experimental and predicted moisture ratio values. The variable N detones the total number of experiments conducted, while the variable z indicates the constant values utilized within the models.

Effective moisture diffusivity

Moisture transport during drying may occur at constant or falling rate periods, governed by complex mass transfer mechanisms. Fick's Second Law is commonly applied to estimate effective moisture diffusivity (D_{eff}) [20] (Eq. 6).

$$\frac{\partial M}{\partial t} = \nabla\left[D_{eff}(\nabla M)\right] \quad (6)$$

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \left(\pi^2 \frac{D_{eff} \times t}{4L^2}\right) \quad (7)$$

Eq. 7 represents Fick's diffusion model for unsteady-state conditions in a thin layer, assuming that moisture is removed by diffusion, shrinkage during drying is ignored, diffusion coefficients, temperature, and equivalent diameter are all constant [20]. L is the half thickness of the sample (m), and n was assumed to be 1 to simplify the calculation. D_{eff} was calculated from the slope of the linear portion of the ln(MR) *vs.* time graph.

Ten commonly used drying models were tested for their compatibility with experimental data, as summarized in Table 1.

Table 1. Mathematical model equations [21, 22]

Name of the model	Model equation
Aghbaslo *et al.*	*MR = exp (−k_1t/(1 + k_2t))*
Alibas	*MR = a.exp ((−kt^n) + bt) + g*
Jena and Das	*MR = a.exp (−kt + b√t) + c*
Lewis	*MR = exp (−kt)*
Logarithmic	*MR = a.exp (−kt) + c*
Midilli & Kucuk	*MR = a.exp (−kt^n) + bt*
Page	*MR = exp (−kt^n)*
Parabolic	*MR = a + bt + ct^2*
Wang and Singh	*MR = 1+ at + b t^2*
Two-term exponential	*MR = a. exp (-kt) + (1-a). exp (-kat)*

a, b, c, g - empirical constants; k, k_1, k_2 - drying rate constants; n - drying exponent; t - time (min).

RESULTS AND DISCUSSION

Table 2 presents the initial and final moisture contents, drying times, and wet basis moisture percentages for squid samples subjected to various pretreatment methods prior to freeze-drying. The results clearly demonstrate that both the type and duration of pretreatment significantly influence the moisture dynamics and drying efficiency of the squid.

Table 2. Drying data of squid

Sample	Initial moisture (kg W / kg DM)	Initial moisture (%)	Drying time (min)	Final moisture (kg W / kg DM)
Control	7.2337	87.85	600	0.6775
B – 1 min	6.4511	86.58	600	0.5490
B – 5 min	5.9741	85.66	540	0.2117
B 10% – 1 min	6.2253	86.16	600	0.3325
B 10% – 5 min	5.7723	85.23	420	0.2208
OD 10% – 5 min	5.7817	85.25	600	0.5080
OD 10% – 10 min	5.1766	83.81	600	0.3218
OD 20% – 5 min	4.6546	82.32	540	0.1874
OD 20% – 10 min	4.1296	80.51	480	0.1359

The control group which did not undergo any pretreatment, exhibited the highest initial moisture content (7.2337 kg W/kg dry matter) and also required the maximum drying time of 600 min to reach a final moisture content of 0.6775 kg water/kg dry matter. This highlights the necessity of pretreatment in accelerating drying and improving efficiency.

Blanching (B – 1 min and B – 5 min) resulted in reduced initial moisture contents compared to the control and substantially improved drying outcomes. Notably, B – 5 min achieved a final moisture content of 0.2117 kg water/kg dry matter in only 540 min, suggesting enhanced moisture removal and internal structure modification that facilitates drying.

Blanching in 10% salt solution (B 10%) demonstrated even more effective results. The B 10% – 5 min sample had one of the lowest initial moisture levels (5.7723 kg water/kg dry matter) and dried in only 420 min, with a final moisture content of just 0.2208 kg water/kg dry matter. This emphasizes the synergistic effect of heat and salt on cellular permeability and water loss.

Osmotic dehydration (OD) treatments showed a more gradual improvement. Samples treated with OD 10% maintained relatively high final moisture levels (0.5080 and 0.3218 kg water/kg dry matter) even after 600 min of drying. However, the OD 20% – 10 min sample showed the best performance among the OD groups, reducing the final moisture content to 0.1359 kg water/kg dry matter in only 480 min, suggesting that higher salt concentrations and longer durations promote better dehydration efficiency.

Figure 1 presents the drying curves of squid samples subjected to various pretreatment methods before freeze-drying. Across all treatments, a continuous decrease in moisture content over time was observed, reflecting the typical drying behavior of biological materials.

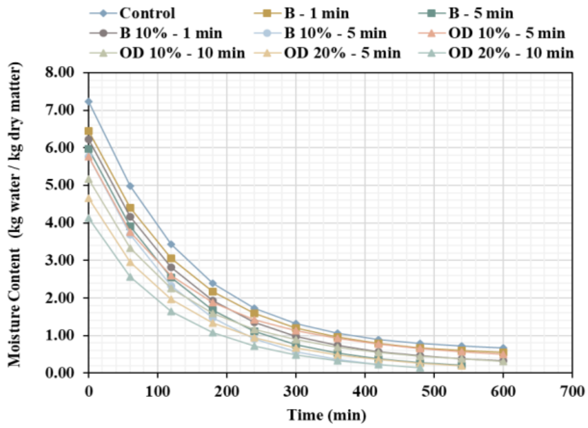

Figure 1. Moisture content *vs* drying rate graph of freeze-drying squid

Figure 2 illustrates the relationship between drying rate and moisture content, providing insight into the drying kinetics and mechanism. All curves show a distinct falling rate period, which is characteristic of freeze-drying.

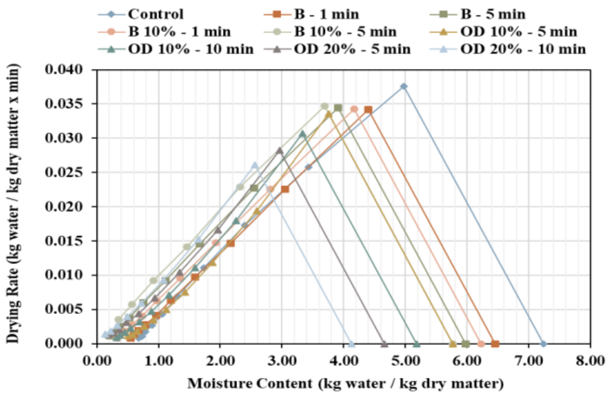

Figure 2. Drying rate *vs*. moisture content graph of freeze-drying squid

This indicates that moisture diffusion from the interior becomes the limiting step after surface moisture is removed. Table 3 demonstrates the best-fitted mathematical models with R^2 values over 0.9998.

Table 3. Mathematical model constants and statistical parameters of freeze-dried squid

S.	Model	R^2	χ^2	RMSE
Contr.	Two-term	0.9999970	0.0000010	0.0005430
	Midilli & Kucuk	0.9999276	0.0000120	0.0025802
	Aghbashlo *et al.*	0.9998512	0.0000176	0.0036992
B - 1 min	Alibas	0.9999992	0.0000001	0.0002499
	Log.	0.9999941	0.0012803	0.0305148
	Midilli & Kucuk	0.9999418	0.0000072	0.0021364
B - 5 min	Alibas	0.9999994	0.0000001	0.0002289
	Two-term	0.9999870	0.0000020	0.0010950
	Midilli & Kucuk	0.9999822	0.0000027	0.0012701
B % 10 - 1 min	Alibas	0.9999997	0.0000001	0.0001680
	Log.	0.9999937	0.0000007	0.0007288
	Midilli & Kucuk	0.9999662	0.0000045	0.0016838
B % 10 - 5 min	Alibas	0.9999957	0.0000011	0.0006543
	Two-term	0.9999850	0.0000030	0.0012310
	Jena & Das	0.9999951	0.0000010	0.0006950
OD % 10 - 5 min	Alibas	0.999997	0.0000001	0.000455
	Two-term	0.999985	0.000002	0.001061
	Aghbashlo *et al.*	0.999939	0.000006	0.002132
OD % 10 - 10 min	Aghbashlo *et al.*	0.999988	0.000001	0.000957
	Two-term	0.999987	0.000001	0.000984
	Midilli & Kucuk	0.999832	0.000019	0.003595
OD % 20 - 5 min	Alibas	0.999999	0.0000001	0.000208
	Two-term	0.999984	0.000002	0.001158
	Midilli & Kucuk	0.999910	0.000012	0.002758
OD % 20 - 10 min	Alibas	0.999998	0.0000001	0.000409
	Midilli & Kucuk	0.999938	0.000009	0.002378
	Log.	0.999905	0.000014	0.002933

Among the evaluated models, the Alibas model demonstrated consistently superior performance across almost all treatment conditions, with exceptionally high coefficients of determination (R^2) and the lowest χ^2 and RMSE values. Particularly in pretreated samples such as B - 5 min, B %10 - 1 min, and OD %20 - 5 min, the Alibas model achieved near-perfect fits (e.g., $R^2 > 0.999999$), indicating its remarkable capability in accurately describing the drying kinetics of squid during freeze-drying.

The Midilli & Kucuk model also performed well, especially in untreated (Control) and short-duration blanched samples (e.g., B - 1 min), though it generally presented slightly higher error metrics compared to Alibas. Nonetheless, it remained one of the more robust models, particularly in treatments involving mild osmotic dehydration and shorter blanching.

Interestingly, the Two-term model showed strong fitting accuracy in certain conditions like Control, B - 5 min, and OD %10 - 10 min, reflecting its adaptability to varying moisture migration patterns. However, in more intensive treatments (e.g., OD %20 - 10 min), its performance was surpassed by Alibas.

CONCLUSION

This study investigated the freeze-drying of squid with pretreatments of blanching, blanching in salt water, and osmotic dehydration. The drying experiments were conducted in 420 - 600 min. The pretreatments with longer durations and/or higher salt concentrations effectively reduced both the initial moisture load and the total drying time required to reach acceptable final moisture levels. Among all, B 10% – 5 min and OD 20% – 10 min stood out as the most efficient strategies in terms of drying performance. Among the mathematical models tested, the Alibas and Midilli & Kucuk models best described the drying kinetics. These findings reinforce the utility of pretreatments and suggest their broader application in seafood preservation technologies.

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