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Determination of Drying Characteristics of Various Seafood by Freeze-drying Method and Investigation of the Effect of Ultrasonic Pretreatment

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Abstract

Freeze-drying properties, effective moisture diffusivity, mathematical modeling, and quality parameters of squid, shrimp, and mussels were investigated. Samples were evaluated as ultrasonic (US) pre-treated and untreated. Drying times were found to be 420 minutes in all samples, US pretreatment decreased the moisture content after drying and increased drying rates. The highest fit for all models was found in the Alibas model. US pretreatment caused a decrease in ash content due to the release of some minerals into the water but did not cause a significant change in protein and crude lipid amounts. US pretreatment increased the lightness of the samples.

Introduction

Seafood encompasses a diverse array of aquatic organisms, each playing unique roles in marine ecosystems and human diets. Blue mussels, European squid, and shrimp are just a few examples of the wide variety of seafood available. These species not only provide sustenance for human populations but also contribute to the intricate web of interactions within marine environments.

Among the diverse range of seafood options, bivalves like blue mussels play a significant role. Blue mussels, scientifically known as *Mytilus edulis*, are prevalent bivalves found in shallow waters along the coasts of Germany (Lemmen, 2018). These smooth-shelled blue mussels have a global antitropical distribution and are ecologically and economically important (Oyarzún et al., 2021). Blue mussels are known to be ecosystem engineers, shaping their environment, and influencing other species within their habitat (Mouritsen et al., 2022).

Moving on to European squid, also known as *Loligo vulgaris*, it is a cephalopod species commonly found in European waters. Squids are known for their high mobility and are important predators in marine ecosystems, preying on various fish and crustaceans (Peixoto, 2023). European squid play a crucial role in marine food webs, serving as both predator and prey. Their abundance and distribution can have cascading effects on the populations of species they feed on and on those that feed on them (Pierri et al., 2006).

Shrimp, another popular seafood item, are crustaceans that are widely consumed worldwide. Shrimp are known for their delicate flavor and are a rich source of protein. In the context of seafood quality, the flavor of shrimp can be a key indicator of freshness, with changes in flavor signaling the onset of spoilage (Liu et al., 2021).

Drying foodstuffs, particularly seafood, is a crucial practice aimed at extending the shelf life of these perishable items. Seafood, being rich in moisture, is highly susceptible to microbial spoilage. Therefore, drying seafood is essential as it reduces the water activity in the product, inhibiting microbial growth and spoilage (Xie et al., 2020). This preservation method helps maintain the quality and safety of seafood products by preventing the growth of harmful microorganisms that can lead to foodborne illnesses (Guizani et al., 2008).

One of the advanced techniques used for drying food products is freeze-drying. Freeze-drying, also known as lyophilization, is a dehydration process that involves freezing the food item and then removing the ice crystals through sublimation, where ice transitions directly into vapor without passing through the liquid phase (Lozinsky, 2018). This method helps retain the nutritional content, flavor, color, and texture of the food product better than traditional drying methods (Zhang et al., 2015).

Due to their minimal physical and chemical deterioration and strong rehydration properties, freeze-dried foods are widely used in prepared foods. Many studies in this field have focused on fruits and vegetables such as strawberries (Zhang et al., 2020), orange puree (Silva-Espinoza et al., 2019), garlic (Feng et al., 2020), tomatoes (Lopez-Quiroga et al., 2020), and pepper (Krzykowski et al., 2018) or meat products such as chicken meat (Cantalejo et al., 2016) and turkey meat (Elmas et al., 2020). While the variety of freeze-dried seafood is quite small in the literature, these studies are generally only focused on the study of drying and rehydration kinetics. These studies focus on shrimp (Ling et al., 2020), sea cucumber (Bai et al., 2012; Mamatov et al., 2019), and various fish (Elavarasan and Shamasundar, 2016; Crapo et al., 2010), while there are very few studies on freeze-drying squid and mussels. Due to the lack of studies on freeze-drying seafood, the aim of this study was to investigate the freeze-drying characteristics of squid, shrimp, and mussels. The effects of ultrasonic pre-treatment on drying kinetics, drying time, and effective moisture diffusivity were investigated. The moisture data obtained in the study were also used to test the fit of some mathematical models for squid, shrimp, and mussel samples. In order to improve the scope of freeze-dried seafood studies, ash, protein, crude lipid, toxic metals, color change, and size change analyses were performed to evaluate the effects of pre- and post-drying and pre-treatment on quality parameters and sample contents.

Materials and Methods

Raw Material Preparation and Determination of the Moisture Content

Squid (origin: China), shrimp (origin: Türkiye), and mussels (origin: Türkiye) were obtained from a local market in Istanbul in October 2021 in frozen form. Before the experiments, the samples, which were kept in a freezer at -18±2℃ (1050T model; Arçelik, Eskişehir, Türkiye), were thawed at +4±2℃ before the test sets, and then they were brought to room temperature in the desiccator. Excess water on the sample surfaces was removed with the help of coarse filter papers. Squid samples were cut into thin strips for drying, while shrimp and mussel samples were processed whole and without shells. For each drying step, squids were grouped as 10.00±0.005 grams, shrimps 10.00±0.010 grams, and mussels 10.00±0.050 grams. Sample weights were measured using a Radwag AS 220.R2 digital balance (Radwag, Radom, Poland) with an accuracy of 0.001 g. In order to determine the moisture content, the samples were dried with a KH-45 hot air-drying oven (Kenton, Guangzhou, China) for 4 hours at 105°C according to the Association of Official Analytical Chemists (AOAC, 2005) procedure.

US Pretreatment and Freeze-Dryer Experiments

At the US pretreatment stage, the samples were subjected to ultrasonic pretreatment at room temperature in distilled water at a ratio of 1/10 (g/mL) for 5 minutes. After the pretreatment, the samples were placed on coarse filter papers and the excess water on their surfaces was filtered. An ultrasonic bath with 1 °C sensitivity and 120 W ultrasonic power (Isolab, Germany) was used for ultrasonic (US) pretreatment. Before the freeze-drying process, the samples were grouped at the desired weights and US pre-treated and unpretreated samples were placed on dryer racks in two parallels.

In order to perform ash, crude lipid, protein, and toxic metal analyses, 5 parallel sets of each sample group were studied in freeze-drying processes. Drying processes were continued until the final moisture of the samples were between 5% and 10% with the data obtained as a result of moisture content determination. In order to study the drying kinetics, the samples were weighed after every 60 minutes of drying and photographed for visual tracking. These processes were carried out in less than 2 minutes in order to prevent the samples from dissolving. The freeze-drying process was carried out in a standard type Labart LFD-10N model freeze dryer (ART Laborteknik, Istanbul, Türkiye) with a cold trap temperature of -56/-80°C, vacuum degree of ≤5 Pa, and power of 950 W.

Drying Curves

The moisture content of the sample decreases as the drying process progresses. Moisture removal is achieved by moisture diffusion from the interior to the surface during the falling-rate period. As a result, moisture is transferred as a mass to the environment around the product. This diffusion mechanism is described by Fick's second law of diffusion (Nag and Dash 2016). During the drying experiments presented in Equations 1, 2, and 3, moisture content (M), moisture ratio (MR), and drying rates (DR) were calculated (Ozyalcin & Kipcak, 2023; Kipcak et al., 2021; Sevim et al., 2019):

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

where M is the moisture content (kg water/kg dry matter), m_w is the water content (kg), m_d is the dry matter content (kg).

$$DR = \frac{M_{t+dt} - M_t}{dt} \quad (2)$$

where DR is the drying rate [kg water/(kg dry matter × min)], M_{t+dt} is the moisture content at drying time $t+dt$ (kg water/kg dry matter), t is the drying time (min).

$$MR = \frac{M_t - M_e}{M_i - M_e} \quad (3)$$

where MR is the moisture ratio (dimensionless), M_t, M_0, and M_e relate to M at any drying time, initial moisture content, and equilibrium moisture content (kg water/kg dry matter), respectively. In the calculations, M_e is generally neglected due to its small amount.

Effective Moisture Diffusivity Calculations

Internal diffusion causes food materials to dry, which usually occurs in the falling-rate period. Based on Fick's second law, which is given in equation 4 explains the drying processes during the falling-rate period (Ozyalcin & Kipcak, 2023; Kipcak et al., 2019):

$$\frac{\partial M}{\partial t} = \nabla\left[D_{eff}(\nabla M)\right] \quad (4)$$

The analytical solution of Fick's diffusion is made with the assumptions that moisture is removed by diffusion, shrinkage during drying is neglected, and diffusion coefficients, temperature, and equivalent diameter are all constant. Fick's law for thin-layer, cylindrical, and spherical models was selected for squid, shrimp, and mussels, respectively, and these equations are given in 5 through 7;

$$MR = \frac{8}{\pi^2}\exp\left(-D_{eff}\,\frac{\pi^2}{4L^2}t\right) \quad (5)$$

$$MR = \frac{8}{\pi^2}\exp\left(-D_{eff}\,\frac{1}{R^2}\frac{\pi^2 \times R^2}{L^2}t\right) \quad (6)$$

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-D_{eff}\,\frac{n^2 \times \pi^2}{R^2}t\right) \quad (7)$$

For squid and shrimp samples, L (m) is half the length of the sample and for shrimp and mussel samples, R (m) is the radius of the sample. To simplify calculations, n is assumed to be 1 in all equations. By taking the natural logarithm (ln) the equations are linearized and from the plot of ln(MR) vs t (s), effective moisture diffusivities (D_{eff}) can easily be calculated.

Mathematical Modelling and Statistical Evaluation

Parameters of models were calculated by applying a non-linear regression procedure based on the Lavenberg–Marquardt algorithm applied by Statistica 8.0 (StatSoft Inc., Tulsa, USA). To determine the best-fitted model, the coefficient of determination R^2, reduced chi-square (χ^2), and root mean square error (RMSE) statistical evaluation methods were applied, and equations are given in equations 8 through 10, respectively. Higher R^2 values and lower χ^2 and RMSE values were accepted as better results in the literature (Kipcak et al., 2019; Sevim et al., 2019; Ozyalcin & Kipcak, 2021):

$$R^2 \equiv 1 - \frac{\sum_{i=1}^{N}(MR_{exp,i} - MR_{pre,i})^2}{\sum_{i=1}^{n}(MR_{exp,i} - \left(\frac{1}{n}\right)\sum_{i=1}^{N} MR_{exp,i})} \quad (8)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N - z} \quad (9)$$

$$RMSE = \left[\frac{1}{N}\sum_{\mathrm{l}=1}^{N}\left(MR_{pre,i} - MR_{exp,i}\right)^2\right]^{1/2} \quad (10)$$

Determination of the Ash Content

Ash analysis can basically be used to determine the mineral content of foods. Accordingly, the change in ash content with the effect of pretreatment and drying was analyzed. The ash content of the dried samples was determined according to the ICC standard No: 104/1 (Williams et al., 2008) by burning them in a Protherm MOS 180/4 model muffle furnace (Alser Teknik Seramik A.S., Istanbul, Türkiye) at 900°C. The samples placed in a ceramic crucible whose base is covered with alumina powder were weighed and placed in the furnace. The furnace was gradually heated to 900°C by 10°C/min and at 900°C the process took about 4 hours. After the samples were removed from the ash furnace, they were taken into a desiccator and allowed to cool at room temperature for an average of 30 minutes. The cooled crucibles were weighed to determine the amount of ash.

Protein Analysis

Since protein content is one of the basic parameters of a food, the effect of drying and pre-treatments on protein content was investigated. Protein amounts of dried samples were determined on the basis of dry matter according to ICC-standard No:105 (Williams et al. 2008). The protein ratio was determined by calculating the total amount of nitrogen found by the Micro Kjeldahl method, multiplied by a factor of 6.25. Potassium sulfate (K_2SO_4, for analysis EMSURE® ACS, ISO, Reag. Ph Euro) (Merck KGaA, Darmstadt, Germany) was used as a catalyst for this process. In addition, a solution of sulfuric acid (H_2SO_4, EMSURE® for 98% analysis) (Merck KGaA, Darmstadt, Germany) was added to the tubes for distillation to take place. The burned samples were transferred to the Buchi KjelFlex K-360 model nitrogen protein distillation unit (BUCHI Labortechnik AG, Flawil, Switzerland). In the distillation process, boric acid (H_3BO_3, for analysis EMSURE® ACS, ISO, Reag. Ph Euro) (Merck KGaA, Darmstadt, Germany) and 40% sodium hydroxide solution prepared with NaOH pellets EMPLURA® (Merck KGaA, Darmstadt, Germany) were used. Finally, the resulting material was titrated with 0.1 M hydrochloric acid (HCl, 37%, for analysis EMSURE® ACS, ISO, Reag. Ph Euro) (Merck KGaA, Darmstadt, Germany) to obtain the nitrogen content. The amount of nitrogen was found by applying equation 11 (Boulos et al. 2020):

$$Nitrogen\ \% = \frac{(V_{HCl} - V_{blank})(mL) \times 14\ \left(\frac{g}{mol}\right) \times M_{Hcl}\left(\frac{mol}{L}\right)}{sample\ weight\ (g) \times 1000\ \left(\frac{mL}{L}\right)} \times 100 \quad (11)$$

where V_{HCl} is the volume of HCl solution used in titration, V_{blank} is the blank volume of the container, 14 is the molar mass of nitrogen, and M_{HCl} is the molarity of the HCl solution. After the nitrogen percentage is found, the protein amount is calculated by using equation 12 by multiplying it with the conversion constant (Boulos et al., 2020):

$$Protein\ \% = Nitrogen\ content\ \% \times 6.25 \quad (12)$$

Crude Lipid Analysis

The amount of crude lipid in the dry products was determined by the E-816 model extraction unit (BUCHI Labortechnik AG, Flawil, Switzerland). The samples to be tested for crude lipids were dehumidified before starting the analysis. Samples weighing between 5 and 10 grams were placed in the cartridge by wrapping them in coarse filter paper after their first weighing was recorded. Extraction was performed in 18 hours by feeding the system an appropriate amount (approximately 1.5 siphons) of chloroform ($CHCl_3$, for analysis EMSURE® ACS, ISO, Reag. Ph Euro) (Merck KGaA, Darmstadt, Germany). Chloroform was separated from the system by distillation. The cartridge was then dried in an oven until it reached a constant weight. The amount of crude lipid extracted from the samples was calculated from the difference between the final weight and the initial weight of the cartridge using equation 13:

$$Crude\ Lipid\ \% = \frac{M_2 - M_1}{m} \quad (13)$$

where "M_1" is the initial weight of the cartridge (g), "M_2" is the post-analysis weight of the cartridge (g), and "m" is the weight of the sample (g).

Toxic Metal Analysis

Seafood can have some nutritional concerns because it can store toxic metals. For this reason, a toxic metal analysis was carried out to determine whether the toxic metal content changes with drying and pre-treatment. Dry samples were dissolved in 6 ml of nitric acid 65% (HNO_3, for analysis EMSURE® Reag. Ph Eur, ISO) (Merck KGaA, Darmstadt, Germany) and 2 ml of hydrogen peroxide 30% (H_2O_2, Perhydrol® for analysis EMSURE® ISO) (Merck KGaA, Darmstadt, Germany) in PTFE containers in the Milestone Ethos Easy microwave system. Then dissolved samples were analyzed with PerkinElmer Optima 2100 DV ICP-OES (PerkinElmer Inc., MA, USA) equipped with an AS-93 autosampler to determine their toxic metal contents (Copper (Cu), Zinc (Zn), Cadmium (Cd), Mercury (Hg) and Lead (Pb)) with the parameters of power of 1.45 kW, a plasma flow of 15.0 L/min, an auxiliary flow of 0.8 L/min, and a nebulizer flow of 1 L/min (Yalcin Gorgulu et al., 2022; Demir et al., 2020).

Color Change Analysis

Before the experiment and after the freeze-drying, color change analysis was performed for each sample from five different regions. The colorimeter device PCE-CSM 1 model (PCE Instruments UK Ltd., Southampton Hampshire, UK) was used for color change analysis. Hunter color analysis is a method that shows the lightness value of the product with +L*, the redness value with +a*, the green value with -a*, the yellowness value with +b*, and the blueness value with -b*. According to these results, how the pretreatment and drying parameters affect the color properties has been interpreted. ΔE (color change) values were calculated by equation 14 (Ozyalcin & Kipcak, 2022);

$$\Delta E = \sqrt{(L_0 - L)^* + (a_0 - a)^* + (b_0 - b)^*} \quad (14)$$

where L*, a*, and b* values are the color parameters of the dried samples while L_0*, a_0*, and b_0* values are the color parameters of the raw samples.

Dimensional Change Analysis

The unpretreated and US pre-treated samples were subjected to dimensional analysis to detect the

size variation between their raw and dry states. This analysis was carried out by measuring the length, width, and thickness of the samples on a millimeter scale. Dimensional analyses were performed using a carbon fiber digital caliper.

Results and Discussion

Drying Curve and Drying Rate Curve Results

Initial moisture contents were calculated as; 5.1802 kg water/kg dry matter for unpretreated squid (83.82% wet basis), 5.7091 kg water/kg dry matter for US pre-treated squid (85.09% wet basis), 3.7971 kg water/kg dry matter for unpretreated shrimp (79.15% wet basis), 4.4029 kg water/kg dry matter for US pre-treated shrimp (81.49% wet basis), 2.4173 kg water/kg dry matter for unpretreated mussels (70.74% wet basis) and 2.6810 kg water/kg dry matter for US pre-treated mussels (72.83% wet basis).

From the results obtained, freeze-drying process was completed in 420 minutes for all unpretreated and pre-treated squid, shrimp, and mussel samples. Samples are given before and after the drying process in Figure 1. In literature studies, drying times for squid were found between 180-300, 150-285, 210-315, 150-285, 150-285, and 150-277 minutes for oven, vacuum oven, oven with ultrasound pretreatment, and vacuum oven with ultrasound pretreatment, and infrared, respectively (Ozyalcin & Kipcak, 2022; 2021). Drying times for shrimp were in the range of 210-330, 110-190 minutes for oven, vacuum oven, and 144 minutes for solar-LPG dryer (Ersan & Tugrul, 2021; Murali et al., 2021). Mussel drying times were 270-120, 570-300, 390-210, and 45-110 minutes for cabinet-type dryer, oven, vacuum oven, and infrared, respectively (Kipcak et al., 2021; 2019). The drying times obtained with the freeze-dryer are noticeably longer compared to the literature. One primary reason for the longer freeze-drying times is the low temperatures at which the process operates. The freeze-drying process typically works at temperatures under the freezing point, which significantly slows down the drying compared to higher-temperature drying methods (Kandasamy & Naveen, 2022).

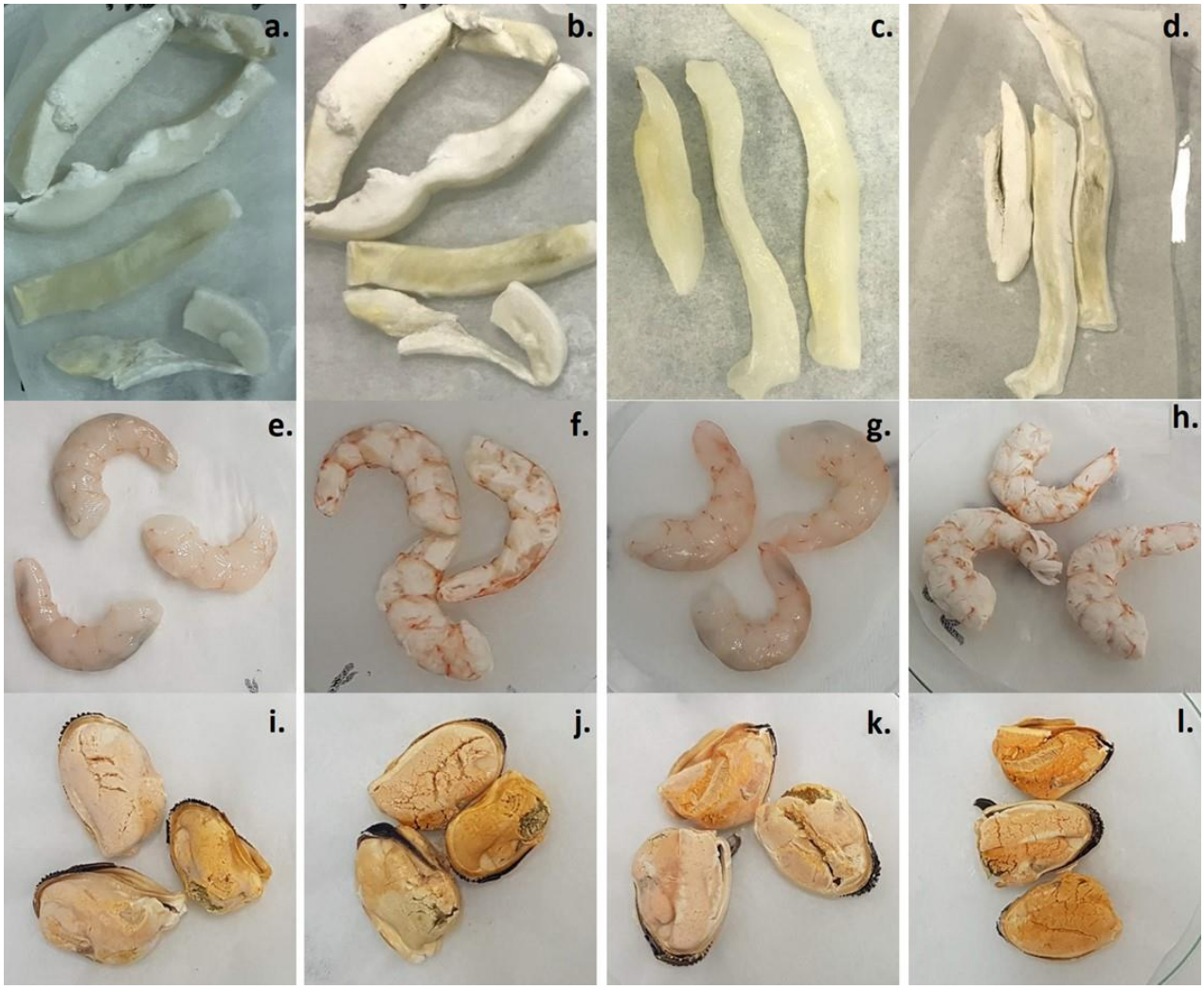

Figure 1. Samples a. raw unpretreated squid, b. dry unpretreated squid c. raw pretreated squid, d. dry pretreated squid, e. raw unpretreated shrimp, f. dry unpretreated shrimp, g. raw pretreated shrimp, h. dry pretreated shrimp, i. raw unpretreated mussels, j. dry unpretreated mussels, k. raw pretreated mussels, l. dry pretreated mussels.

Final moisture contents for dry samples were found as; 0.5290 kg water/kg dry matter for unpretreated squid, 0.2476 kg water/kg dry matter for US pre-treated squid, 0.2037 kg water/kg dry matter for unpretreated shrimp, US for pre-treated shrimp calculated as 0.3787 kg water/kg dry matter, 0.1063 kg water/kg dry matter for unpretreated mussels, and 0.1725 kg water/kg dry matter for US pre-treated mussels. The change in the moisture content of the samples with respect to time (min) is given in Figure 2.

Falling-rate periods were found between the drying rates of; 0.0244 – 0.0052 kg water/kg dry matter × minute for unpretreated squid, 0.0284 – 0.0052 kg water/kg dry matter × minute for US pre-treated squid, 0.0194 – 0.0032 kg water/kg dry matter × minute for unpretreated shrimp, 0.0240 – 0.0038 kg water/kg dry matter × minute for US pre-treated shrimp, 0.0136 – 0.0016 kg water/kg dry matter × minute for unpretreated mussels and 0.0147 – 0.0021 kg water/kg dry matter × minute for US pre-treated mussels.

The drying rate curves of the samples of the unpretreated and US pre-treated samples are shown also in Figure 2. According to the curves obtained only a falling-rate period was seen. Hence, the initial humidity was higher in the US pre-treated samples. The pre-treated samples entered the falling-rate drying period earlier because of the higher moisture content. Furthermore, the US pretreatment application increased the drying rates.

Effective Moisture Diffusivity Results

Fick's second law was applied to unpretreated and US pre-treated samples. From the slope of the plot of ln(MR) versus time (s), D_{eff} values were calculated as 3.17×10^{-10} m^2/s for unpretreated squid, 4.27×10^{-10} m^2/s for US pre-treated squid, 7.03×10^{-11} m^2/s for unpretreated shrimp, US pre-treated 5.89×10^{-11} m^2/s for treated shrimp, 1.30×10^{-10} m^2/s for unpretreated mussels, and 1.49×10^{-10} m^2/s for US pre-treated mussels.

Compared with the literature, D_{eff} values were found consistent with D_{eff} values in various seafood drying studies. As examples, D_{eff} values in the drying of squid found between 9.81×10^{-11} - 1.32×10^{-10} m^2/s in oven, 6.36×10^{-11} - 1.67×10^{-10} m^2/s in vacuum-oven, 8.75×10^{-11} - 1.05×10^{-10} m^2/s in oven with ultrasound pretreatment, 7.66×10^{-11} - 1.84×10^{-10} m^2/s in vacuum-oven drying with ultrasound pretreatment (Ozyalcin & Kipcak, 2022), 6.57×10^{-10} - 1.35×10^{-9} m^2/s in infrared drying, and between 1.25×10^{-8} - 5.62×10^{-8} m^2/s in microwave drying (Ozyalcin & Kipcak, 2021). D_{eff} values in the drying of shrimp were found between 1.46 10^{-8} - 2.8×10^{-8} in oven, 3.68×10^{-8} - 5.49×10^{-8} m^2/s in vacuum-

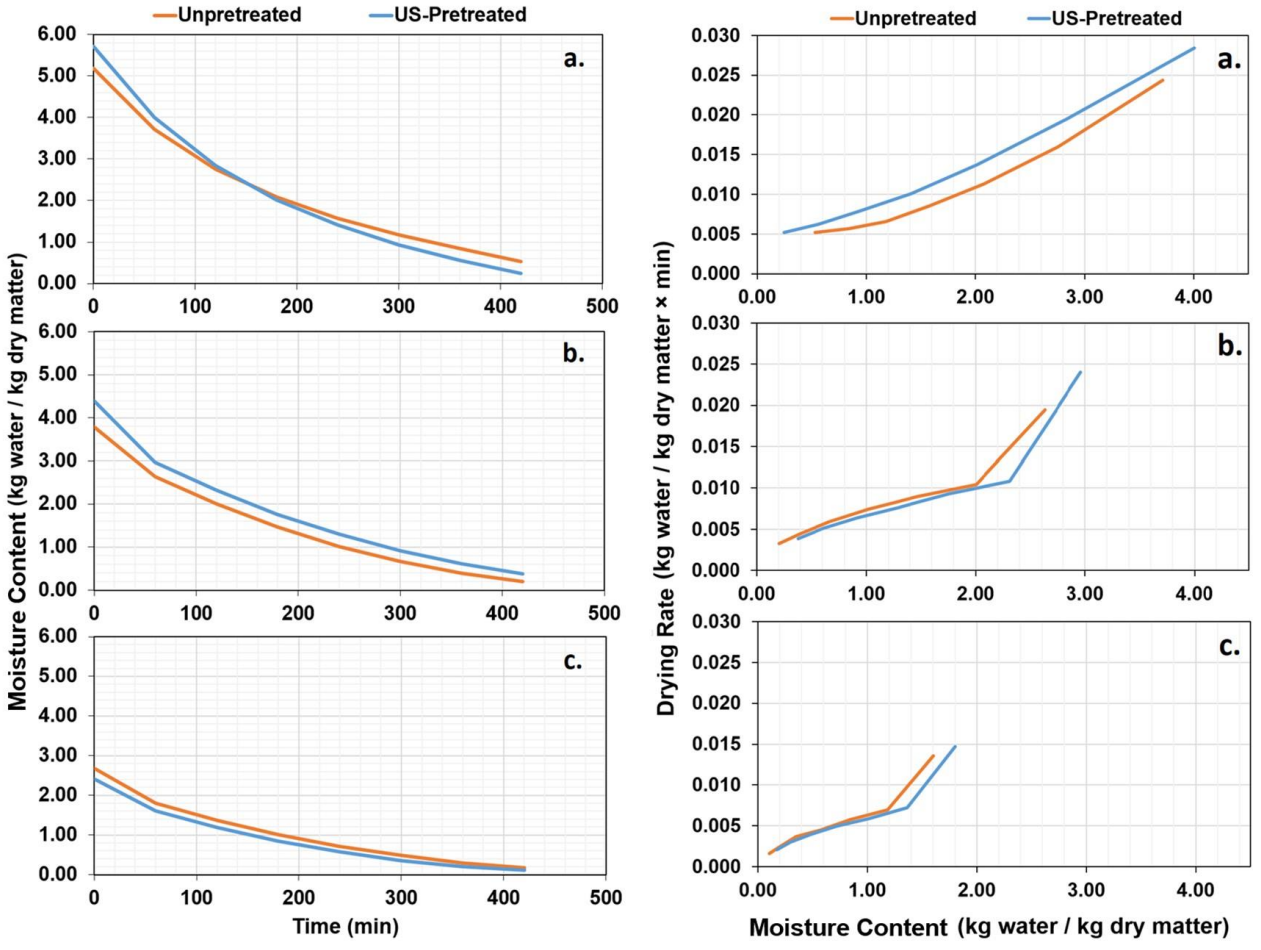

Figure 2. Moisture content and drying rate curves of a. squid, b. shrimp and c. mussels.

oven (Ersan & Tugrul, 2021), and as 1.04×10^{-9} m^2/s in solar LPG dryer (Murali et al., 2021). D_{eff} values in the drying of mussels were found between 1.89×10^{-9} - 4.94×10^{-9} m^2/s in cabinet-type dryer, 0.89×10^{-9} - 1.63×10^{-9} m^2/s in oven, 1.17×10^{-9} - 2.28×10^{-9} × m^2/s in vacuum oven (Kipcak et al., 2021), and between 4.24×10^{-9} - 1.10×10^{-8} m^2/s in infrared dryer (Kipcak et al., 2019).

Furthermore, all calculated values are in the range of 10^{-8} to 10^{-12} m^2/s, as described in the literature for diffusion coefficients of biological materials (Acar et al., 2023).

Mathematical Modelling and Statistical Results

Squid (origin Drying data (MR) of unpretreated and pre-treated samples of squid, shrimp, and mussels dried by freeze-drying method were applied to various mathematical models of Aghbaslo et al., Alibas, Henderson and Pabis, Two-Term, Jena & Das, Lewis, Logarithmic, Midilli & Kucuk, Page, Parabolic, Verma et al., Wang & Singh, and Weibull. The highest R^2 and the lowest χ^2 and RMSE values and model constants of these models are given in Table 1.

When the model parameters were evaluated, Alibas and Midilli & Kucuk. models showed the best fit with all samples, respectively. When the unpretreated squid data were examined, the R^2 values of 0.999996 and 0.999884, reduced χ^2 values of 0.000273 and 0.000019, and RMSE values of 0.010119 and 0.003079 were found for Alibas and Midilli & Kucuk models, respectively. For the US pre-treated squid samples R^2 values of 0.999998 and 0.999966, reduced χ^2 values of 4E-07 and 0.000006, and RMSE values of 0.000371 and 0.001787 were found for Alibas and Midilli & Kucuk models, respectively.

When the unpretreated shrimp data were examined, the R^2 values of 0.999692 and 0.999503, reduced χ^2 values of 0.000019 and 0.000046, and RMSE values of 0.004345 and 0.005522 were found for Alibas and Midilli & Kucuk, respectively. For the US pre-treated shrimp samples, the R^2 values of 0.999710 and 0.999630, reduced χ^2 values of 0.000064 and 0.000066, and RMSE values of 0.005326 and 0.006068 were found for Alibas and Midilli & Kucuk models, respectively.

When unpretreated mussel data were examined, the R^2 values of 0.999690 and 0.999430, reduced χ^2 values of 0.000078 and 0.000108, and RMSE values of 0.005394 and 0.007353 were found for Alibas and Midilli & Kucuk models, respectively. For the US pre-treated mussel samples, the R^2 values of 0.999721 and 0.999576, reduced χ^2 values of 0.000081 and 0.000092, and RMSE values of 0.005504 and 0.006789 were found for Alibas and Midilli & Kucuk models, respectively.

Alibas and Midilli & Kucuk were found to be the most compatible models among many models in the literature on the drying of squid, shrimp and mussels. For example, Midilli & Kucuk model was the most compatible model in oven, vacuum oven with ultrasound pretreatment (Ozyalcin & Kipcak, 2022), infrared and microwave (Ozyalcin & Kipcak, 2021) drying of squid, vacuum oven drying of shrimp (Ersan & Tugrul, 2021) and cabinet-type, oven, vacuum oven (Kipcak et al., 2021) and infrared (Kipcak et al., 2019) drying of mussels. The Alibas was the most compatible model in ultrasound pretreatment oven drying of squid (Ozyalcin & Kipcak, 2022) and oven drying of shrimp (Ersan & Tugrul, 2021).

Content Analyses of Ash, Protein, Crude Lipid, and Toxic Metal Results

The ash, protein, crude lipid, and toxic metal contents of the freeze-dried samples are given in Table 2.

It is seen that the ash content was 5.32% and 2.64% by mass in unpretreated and pre-treated squid samples, 6.77% and 5.48% by mass in unpretreated and pre-

Table 1. Mathematical modeling parameters and statistical evaluation results

	Unpretreated Squid		Unpretreated Shrimp		Unpretreated Mussels	
Parameters	Alibas	Midilli & Kucuk	Alibas	Midilli & Kucuk	Alibas	Midilli & Kucuk
a	0.573860	1.000550	3.902190	0.998790	3.882640	0.998830
b	-0.000810	-0.000170	0.001460	-0.000340	0.001660	-0.000300
g	0.426110	–	-2.903380	–	-2.883800	–
k	0.008900	0.009460	0.003650	0.010460	0.004390	0.012060
n	0.994980	0.862510	0.817910	0.839020	0.801530	0.838660
R^2	0.999996	0.999884	0.999692	0.999503	0.999690	0.999430
χ^2	0.000273	0.000019	0.000019	0.000046	0.000078	0.000108
RMSE	0.010119	0.003079	0.004345	0.005522	0.005394	0.007353
	US-Pretreated Squid		US-Pretreated Shrimp		US-Pretreated Mussels	
Parameters	Alibas	Midilli & Kucuk	Alibas	Midilli & Kucuk	Alibas	Midilli & Kucuk
a	0.746820	1.000380	3.515510	1.158820	3.653480	1.108173
b	-0.000590	-0.000190	0.000530	-0.000500	0.001060	-0.000380
g	0.253200	–	-2.356700	–	-2.545300	–
k	0.007600	0.007780	0.007540	0.019960	0.005720	0.015170
n	0.988710	0.924090	0.679500	0.698960	0.747530	0.771653
R^2	0.999998	0.999966	0.999710	0.999630	0.999721	0.999576
χ^2	0.000001	0.000006	0.000064	0.000066	0.000081	0.000092
RMSE	0.000370	0.001790	0.005326	0.006068	0.005504	0.006789

treated shrimp samples, 18.38% and 18.75% by mass in unpretreated and pre-treated shrimp samples. When the effect of US pretreatment on the ash content was examined, it was determined that a 2.68, 1.29, and 0.37% decrease was observed in the ash content in the squid, shrimp, and mussels, respectively. The decrease in ash content can be interpreted as the inorganic substances in the samples passing through the pores that expand under the effect of ultrasound waves into the water, which is the US pretreatment medium. This situation was not seen in the mussel samples, but the ash contents were quite close and the difference is acceptable.

From the crude lipid analysis results, it was determined that crude lipid content was 4.80% and 6.25% in squid samples, 8.75% and 9.50% in shrimp samples, and 17.00% and 15.39% in mussel samples, by mass for unpretreated and pre-treated samples, respectively. When the data were examined in the pretreatment criterion, it was observed that there was an increase of 1.45% in crude lipid content in the pre-treated squid samples, 0.75% in the shrimp samples, and a decrease of 1.61% in the mussel samples. The reason for this is thought to be the unique body integrity and physicochemical properties of organic samples such as the protein content. The fact that the crude lipid amounts for the pretreated and unpretreated samples show a very low percentage change can be interpreted as US pretreatment does not cause a change in the crude lipid amount of the sample.

Cadmium, mercury, and lead ions were detected in undetectable (N.D.) levels in all samples when the toxic metal content was analyzed. Copper ions were detected in some squid samples, while variable quantities of zinc ions were found in all samples. When the copper and zinc ion content of the samples was analyzed, it was revealed that the amount of metal ions in the unpretreated samples decreased, whilst the ion amounts in the pre-treated samples were preserved.

Quality Analyses of Total Color Change and Dimension Results

Table 3 shows the color measurements for the squid and shrimp samples, together with the standard deviation values. Since the mussel samples contain colors such as white, yellow, orange, green, and black in their bodily integrity, the mussel samples were not assessed since the color change analyses employed did not produce very healthy results.

When color values were assessed, all squid samples showed an increase in lightness, redness, and yellowness values after drying, however pre-treated squid samples had higher lightness, redness, and yellowness values than unpretreated samples. It was revealed that pre-treating raw squid samples raised the values of lightness, redness, and yellowness. When the shrimp samples were examined, it was discovered that after drying, the lightness and yellowness values increased while the redness values decreased. Furthermore, it was revealed that pre-treating raw shrimp samples lowered the lightness, redness, and yellowness values. In the pre-treated shrimp samples, however, the drying impact resulted in an increase in lightness, redness, and yellowness values.

Color change values (ΔE) were calculated by taking the colors of unpretreated raw samples as reference. Accordingly, the calculated ΔE values should be considered as the divergence value from unpretreated raw samples. When the color change values of the

Table 2. The compositions of the freeze-dried samples of squid, shrimp and mussels

Sample	Moisture % (wet basis)	Ash % (dry basis)	Protein % (dry basis)	Crude Lipid % (dry basis)	Cu (mg kg^{-1}) (dry basis)	Zn (mg kg^{-1}) (dry basis)
Unpretreated Squid	83.82	5.32	64.67	4.8	2.42±0.13	9.31±0.44
US Pre-treated Squid	85.09	2.64	64.43	6.25	23.88±1.27	41.33±1.95
Unpretreated Shrimp	79.15	6.77	79.49	8.75	N.D.(<0.24)	5.69±0.27
US Pre-treated Shrimp	81.49	5.48	81.97	9.5	N.D.(<0.99)	29.78±1.40
Unpretreated Mussels	70.74	18.38	52.27	17	N.D.(<0.23)	8.88±0.42
US Pre-treated Mussels	72.83	18.75	50.8	15.39	N.D.(<0.98)	40.50±1.91

N.D.: not detected

Table 3. Color values for the freeze-dried samples

Sample	**L***	**a***	**b***	**ΔE**
Unpretreated Squid - Raw	49.90±1.89	-1.99±0.18	0.95±0.76	–
Unpretreated Squid - Dry	85.11±2.53	1.67±0.62	10.50±1.72	37.15±0.47
Pre-treated Squid - Raw	53.45±2.38	-0.94±0.66	2.20±1.12	4.37±0.21
Pre-treated Squid - Dry	86.50±2.28	1.87±0.98	9.77±1.05	39.04±0.14
Unpretreated Shrimp - Raw	67.88±1.96	3.33±0.88	0.01±0.71	–
Unpretreated Shrimp - Dry	84.28±2.37	0.30±1.50	9.69±1.17	19.28±0.48
Pre-treated Shrimp - Raw	53.74±2.45	1.36±0.96	-2.21±0.41	14.44±0.31
Pre-treated Shrimp - Dry	85.00±2.24	2.77±1.43	8.49±1.19	19.11±0.45

samples were examined, it was observed that the ΔE value for the squid samples was 4.37 ± 0.21 in the US pre-treated raw samples, 37.15 ± 0.47 in the unpretreated dry samples, and 39.04 ± 0.14 in the US-treated dry samples. It can be interpreted that the change in US pre-treated raw samples is mainly due to the increase in the lightness/darkness value. For shrimp samples, the ΔE value was found to be 14.44 ± 0.31 in US pre-treated raw samples, 19.28 ± 0.48 in unpretreated dry samples, and 19.11 ± 0.45 in US-treated dry samples. Although the amount of change in the US pre-treated raw samples was high, it was observed that the difference between the dry samples was quite low.

A dimensional analysis was conducted to assess the effect of the freeze-drying on sample dimensions. The evaluation was based on the average dimensions of two parallel samples that were utilized as a reference during the measurements. When the results were examined, the mean percentage size changes after drying in unpretreated squid samples were seen as 23.9% in thickness, 11.4% in length, 18.5% in width, and in pre-treated squid samples, 10.5% in thickness, 13.1% in length and 21.2% in width. As for the shrimp samples, size changes after drying were 6.7% in head thickness, 6.25% in tail thickness, 2.3% in length, and for pre-treated shrimp samples, 6.7% in head thickness, 22.2% in tail thickness, 1.2% in length. No change was recorded in the width of the shrimp samples. For the mussel samples, size changes after drying were 1.1% in thickness, 0.7% in length, 0.7% in width, and in pre-treated mussel samples, 0.3% in thickness, 0.5% in length and 0.7% in width were observed. When the volumetric variation of the samples was calculated, it was discovered that the pretreatment was very successful in maintaining the size of the shrimp and mussel samples but had an adverse effect on the shrimps.

Conclusions

In this study, freeze-drying characterizations of squid, shrimp, and mussels with and without ultrasonic pretreatment were investigated. According to the results obtained, the initial moisture level of the US-pre-treated samples was found to be higher. In addition, while the same drying time was observed for all samples, the drying rates in the US pre-treated samples were seen to be higher and the effective moisture diffusion values in US pre-treated samples were found to be greater. Among the mathematical models, Alibas model was determined as the best model. Among the analyses applied to determine the final product quality, the amount of ash in the US pre-treated samples was found to be fairly low compared to the unpretreated samples. The effect of pretreatment had no major effect on protein, crude lipid, or toxic metal content in the samples. According to the color values, US pretreatment resulted in an increase in lightness and yellowness in squid samples, as well as an increase in lightness in shrimp samples and a decrease in yellowness and redness values. The variations in the raw and post-freeze-drying dimensions of the samples were significantly small, and the US pretreatment had a reducing influence on the size changes of the samples during the freeze-drying process, according to the dimensional analysis.

Ethical Statement

Not applicable.

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Author Contribution

ZOO, EG, DU, and FB carried out the experiments, OS, ID, NC, ED and ASK analyzed the data and wrote the MS, ASK supervised the work and edited the manuscript.

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

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