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RESEARCH ARTICLE

FISH PRE-TREATED WITH SALT BRINE: PROCESS STUDY AND DRYING KINETICS

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Abstract

This work is part of a study for the conservation of fish products through solar drying. The grey seabream is dried after a pre-treatment of 16 hours in a salt brine under two conditions: on a rack in open air and in a solar dryer. The tests were carried out under average irradiance conditions of 592.76 W/m², an average ambient temperature of 30°C and an average air temperature in the dryer of 50°C. The results obtained, allowed us to reach a final humidity of 32% from an initial humidity of 65% in a wet basis. The drying was processed in 15 hours, (i.e. two days in the dryer) and 24 hours (i.e. three days in the open air). The modeling of the drying kinetics of the grey sea bream is carried out from empirical or semi-empirical models taken from the previous works. Several criteria were defined for the choice of the two-term model as being the one that can describe in the best way, the drying of the fish in both conditions. The effective diffusivity was determined using Fick's diffusive model whose solution is given by Crank, so that the logarithm of the reduced moisture allows us to find effective diffusivities for fish of 9.88823 10-7 (m²/s) and 1.72534 10-6 (m²/s) for open-air and in dryer drying respectively.

Introduction:-

Nomenclature:

a,b,c,g, k = model constant

D_{eff} = effective diffusivity (m²/s)

L= product thickness (m)

t= drying time (s)

r^2 = correlation coefficient

X = fish moisture content

X_r = reduced moisture

$X_{rpre,i}$ = predicted moisture content

$X_{r\exp,i}$ = experimental moisture content

Z = number of constant

RMSE= root mean square errors

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χ^2 = the reduced square

Introduction:
Fish is a highly perishable species that is mainly made up of water, with an initial moisture content of between 65% and 80% depending on the species. This available water favors the development of micro-organisms and bacteria, which can cause its deterioration if it is not well preserved.

Several techniques are used for the preservation of fishes in order to extend the consumption over time. One of these techniques is the solar drying.

Solar drying is a process that extracts some of the moisture content from the fish, allowing it to be kept at ambient temperature [14]. According to Jason, the final moisture content after drying is 35% for salted fish [8].

Local drying is a purely traditional technique and consists of exposing the fish to the sun on high racks (Fig.1), which can cause considerable disadvantages. Due to the dust, the bad weather, the bacteria and the high ambient humidity; the drying process is poorly performed and the product deteriorates easily [7][9]. The fish first undergoes fermentation in a salt brine, which gives it a special flavor. However, there is also the phenomenon of osmosis that takes place in this brine. The salt entering the fish inhibits the action of enzymes, which slows down the deterioration of the fish.

Fig.1: local solar drying

Several works have been carried out in the context of fish drying, among them we have Lamsyehe et al [10], who studied the drying kinetics of anchovy under three different temperatures, he also found an optimal value of water activity for anchovy conservation of 0.3. Bahammou et al [24], valorized the by-products of sardine waste by physical treatment under natural and forced convection solar drying. They concluded that Increasing the temperature and drying air flow rate reduces the moisture content of the sardine heads. Mehta and al [18], realized a drying of fish in a mixed dryer, from a moisture content of 89% to a final moisture content of 10% in 18 hours, and found an effective diffusivity for the fish of 1.53 10-7 m²/s.

Modelling of drying kinetics is a process in which, using empirical or semi-empirical models, makes possible the describing of the drying process of certain products under well-defined conditions. Most of the studies that have been conducted in this direction have dealt with the drying of products such as mango [22], banana [23], marjoram leaves [2], beef [4], pepper [25], potato [1], sweet cherry [20]. Other authors have tried to study the effective diffusivity of several products while showing its dependency on temperature ([15],[16]), but also on drying devices [3], on drying thermal power [1], and on irradiance [17]. There is little work on the drying of fish pretreated with salt brine, in addition to the fact that it is the most locally used pre-treatment method. It is within this framework that we propose to make a study of this drying using a solar drying device.

The objective of this work is to study the drying of the grey sea bream pre-treated with a salt brine, to make a comparison of the two drying modes, i.e. drying in the open air and in the dryer and show the influence of the product temperature on the drying kinetics. We aim to model the drying kinetics of reduced moisture using empirical models from previous works, and to determine the effective diffusivity of the fish for the two types of drying using Fick's diffusive model.

Materials and Methods:-

Experimental device:

For our tests we will use two devices:

A raised drying rack (fig.2a) consisting of a wooden frame with a net as a support, used in the local drying of fish. Here the fish is deposited on these nets in the open air in contact with the sun and the wind.

A mixed tunnel solar dryer with forced convection (fig.2b) which is a modern device for drying. This dryer consists of a photovoltaic module, an absorber and a drying cabin. The module is responsible for converting solar radiation into electrical energy to operate the fans. The latter are responsible for sending the air to the collector where it is heated before entering the drying cabin. This moisture-laden air is exhausted through an opening in the cabin.

(a) : drying rack (b) : solar dryer

Fig 2: Drying device

Experimental procedure:

The tests were carried out at the CERER (Centre for Studies and Research on Renewable Energies) during the months of November and December. Fresh fish was purchased from fishermen in the locality of Yarakh, not far from the study site, latitude 14.72 - longitude -17°.44 Checks were carried out on the physical quality of the product (color, texture, etc.).

Stainless steel knives are used for trimming, i.e. scaling and evisceration. After trimming, the fish are pre-treated with salt brine for 16 hours, before undergoing drying. Drying is done on both devices, i.e. the drying rack, where the fish is placed on the rack in the open air in contact with the sun and wind and in the solar dryer. During the drying process, three measuring tools are used:

1. a solarimeter (model: PYR 1307, accuracy: ±5%) is used to measure the irradiation;
2. a thermochromic temperature probes (model DS1922T, accuracy: 0.5°C) for the measuring of the temperature of the fish;
3. a thermocouple (model: PCE-T390, accuracy: 0.2%) with three probes placed inside and outside the dryer to measure the temperatures of the ambient air and the inside of the dryer.

Several samples are used as controls on the racks and in the dryer. Weighings are carried out using an electronic balance (model: CX 265, accuracy: 0.01mg) before and during the drying procedure at one-hour intervals. At the end of drying, the samples are placed in a drying oven at 105°C for 24 hours to determine their anhydrous masses.

Mathematical modeling:

Five empirical or semi-empirical models defined in Table 1 [21] [10] [2] and [12], are used to smooth the experimental curves of the reduced moisture over time to predict fish drying. This smoothing was performed using the Levenberg-Marquardt nonlinear regression method on Origin pro 9 .1.

Table 1: mathematical models

Number	Model name	Expression
1	Newton	$X_r = \exp(-kt)$

2	Page	$X_r = \exp\left(-kt^n\right)$
3	Logarithmic	$X_r = a\exp\left(-kt\right)+c$
4	Wang and Singh	$X_r = 1+at+bt^2$
5	Two-term	$X_r = a\exp\left(-kt\right)+b\exp\left(-gt\right)$

Criteria for choosing the model:

In order to obtain an appropriate model to describe the drying of the grey sea bream, the criteria of highest correlation coefficient, the minimum roots mean square error and the minimum reduced square respectively defined by equations (1), (2) and (3) were chosen [22][2].

Correlation coefficient (r²) given by equation (1)

$$r^2 = \frac{\sum_{i=1}^{N}\left(X_{rpre,i} - X_{r\exp,i}\right)^2}{\sum_{i=1}^{N} X_{r\exp,i}^2} \qquad (1)$$

Roots mean systematic error (RMSE) defined by equation (2).

$$RMSE = \frac{1}{N}\sum_{i=1}^{N}\left(X_{rpre,i} - X_{r\exp,i}\right) \qquad (2)$$

χ -reduced square given by equation (3).

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(X_{rpre,i} - X_{r\exp,i}\right)^2}{N-Z} \qquad (3)$$

Where $X_{r,pre,i}$ is the predicted relative humidity, $X_{r,\exp,i}$ the experimental relative humidity, and Z is the number of constants for each regression model.

3.2 Determining effective diffusivity

The effective diffusivity is determined from Fick's Law of Moisture Transfer [10]. It is defined by equation [4].

$$\frac{\partial X}{\partial t} = D_{eff}\nabla^2 X \qquad (4)$$

The solution of the equation is given by Crank in one dimension [18].

$$X_r = \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j-1)^2}\exp\left[-(2j-1)^2\frac{\pi^2 D_{eff} t}{L^2}\right] \qquad (5)$$

With L the thickness of the product

Since the drying time is long, the other terms of the series can be neglected in front of the first term. This leads us to equation (6).

$$X_r = \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 D_{eff} t}{L^2}\right) \qquad (6)$$

The effective diffusivity is obtained by making the logarithm of the reduced humidity given by equation (7).

$$\ln(X_r) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D_{eff} t}{L^2} \qquad (7)$$

With Deffwhich is determined using the slope of the experimental results.

Results and discussion:-

Variations in ambient air temperature, dryer interior temperature and irradiance are shown in Figure 3. At the beginning of the day, the two temperatures are the same and then there is a considerable difference as the solar radiation increases. The ambient temperature changes as the irradiance changes, while the temperature of the air inside the dryer increases with the radiation, but remains constant for a period of time before decreasing. The explanation is that in the dryer, the solar radiation is converted into heat which is retained for a certain time before decreasing, due to the thermal insulation of the dryer.

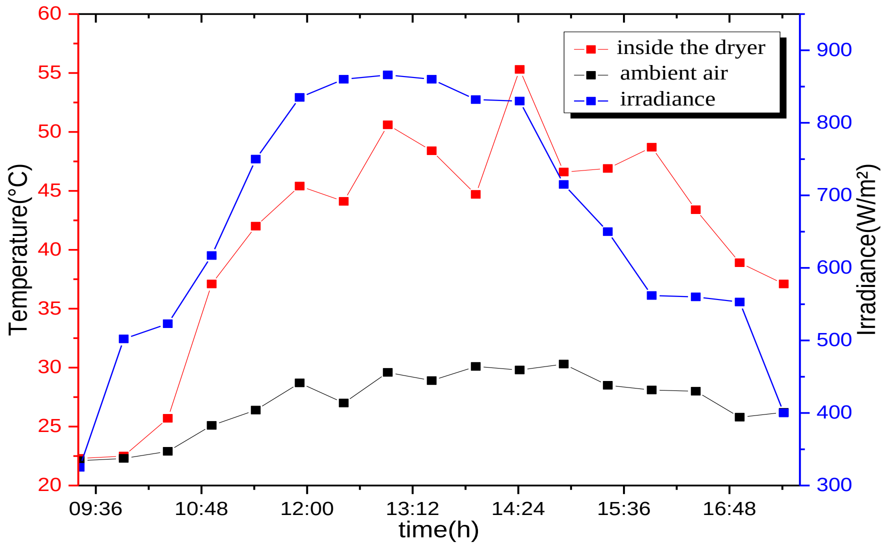
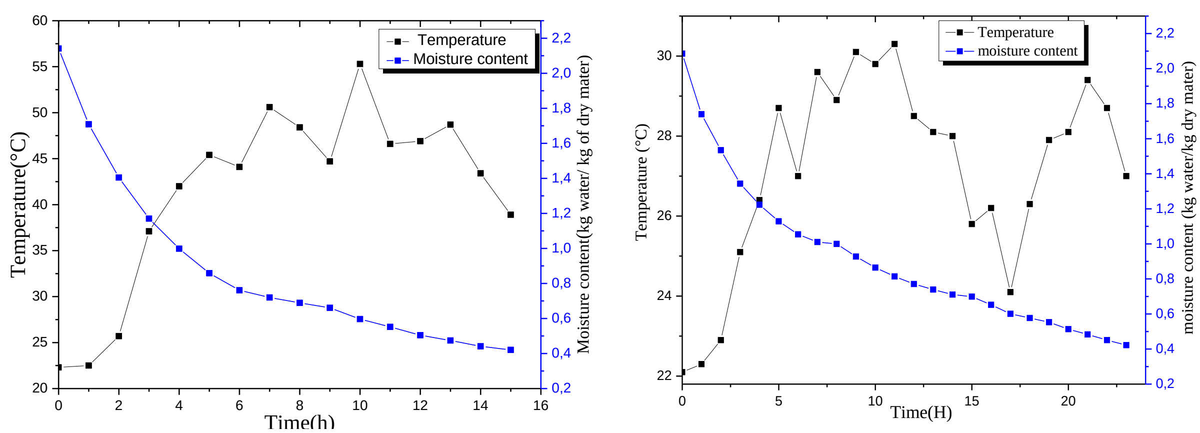


Fig 3: Variation in climatic conditions

In Figure 4, the representation of the drying curve of the fish over time showed two stages in the drying process: a first stage that lasts six hours in the dryer fig.4a and five hours in the open-air fig.4b. During that experiment, one notes a rapid drying of the moisture of the product which coincides with the increase of its temperature. On the other hand, there is a slowing down of the drying speed after six hours in the dryer and five hours in the open air, even at a fairly high temperature. The phase of heating was not observed at the beginning of the drying process, only the decreasing phase was noted, the first six hours corresponding to the elimination of free water. After the six hours, it is the bound water that escapes from the product. The extraction of this water is done by diffusion from the inside of the product to the surface and this diffusion requires a fairly high temperature. The higher the temperature, the shorter the drying time [19].



(a): In the dryer (b): In the open air

Fig 4: Influence of temperature on the drying of the product

Drying curves:
The variation in product moisture content in the two drying modes is shown in Figure 5, which shows the drying that takes place during drying; a comparison between the two types of drying shows a higher drying speed in the dryer than in the open air. The drying time is shorter in the dryer with only 15 hours out of 24 hours in the open air.

This is explained by the fact that the temperature inside the dryer is higher and the increase in temperature favors faster drying leading to a shorter drying time, whereas in the open air the temperature is lower, drying depends on the wind speed, hence the slowness of the drying process.

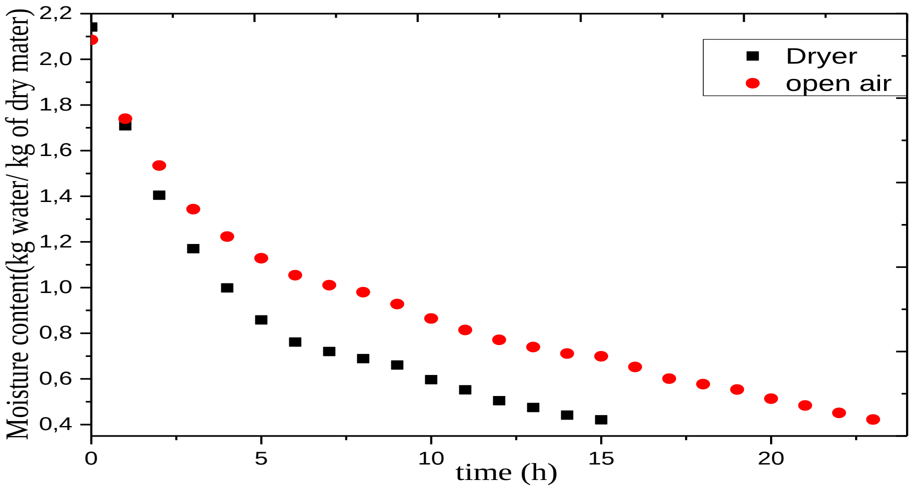


Fig.5: Decrease in fish humidity as a function of time in the dryer and in the open air.

Modeling of drying kinetics:
In order to predict the behavior of sea bream during the drying process, the representation of reduced humidity as a function of time was made for different drying conditions. Smoothing was performed using five empirical models selected from the literature.

The parameters of each model were identified and the statistical results extracted using Origin pro 9.1 software. The statistical results of the models such as correlation coefficient (r^2), reduced square values (χ^2), and root mean square errors (RMSE) are summarized in Table 2.

Table 2: model coefficients

Model		Coefficient	r^2	*RMSE*	χ^2
Newton	Open air Dryer	$K = 0,12287$ $K = 0,21936$	0,94996 0,98054	0,06583 0,02122	0,00286 0,00141
Page	Open air	K= 0,30385 n= 0,80836	0,99609	0,00398	2,84282 10^{-4}
	Dryer	K= 0,22521 n= 0,73225	0,99378	0,00783	3,5607 10^{-4}
Logarithmique	Open air	a= 0,84301 k= 0,14175 c= 0,08297	0,97986	0,02419	0,00115
	Dryer	a= 0,91035 b= 0,26933 c= 0,07569	0,99464	0,00506	3,89377 10^{-4}
Wang	Open air	a= -0,09697 b= 0,00264	0,8919	0,13603	0,00618

And Singh	Dryer	a= -0,16253 b= 0,00708	0,92848	0,07278	0,0052
Two-Term	Open air	a= 0,27559 b= 0,72761 g= 0,08712 k= 0,72013	0,99616	0,0044	2,19846 10^{-4}
	Dryer	a=0,50657 b=0,4976 g=0,46215 k=0,12784	0,99759	0,00210	1,75148 10^{-4}

The criteria of high correlation coefficient (r2), RMSE and χ^2 low made it possible to bring out two models which give a good fit. The Two-Term model with statistical results of $r^2 = 0,99616$, $RMSE = 0,0044$, $\chi^2 = 2,19846\ 10^{-4}$, for open air and $r^2 = 0,99759$, $RMSE = 0,0044$, $\chi^2 = 1,7514810^{-4}$, for the dryer, and the page model with statistical results of $r^2 =\ 0,99609$, $RMSE = 0,00398$, $\chi^2 = 2,8428210^{-4}$, for open air and $r^2 = 0,99378$, $RMSE = 0,00783$ et $\chi^2 = 3,560710^{-4}$ for the dryer.

The comparison between these two models according to the criteria set out in paragraph 3.1 made it possible to select the Two-Term model for the two drying modes.

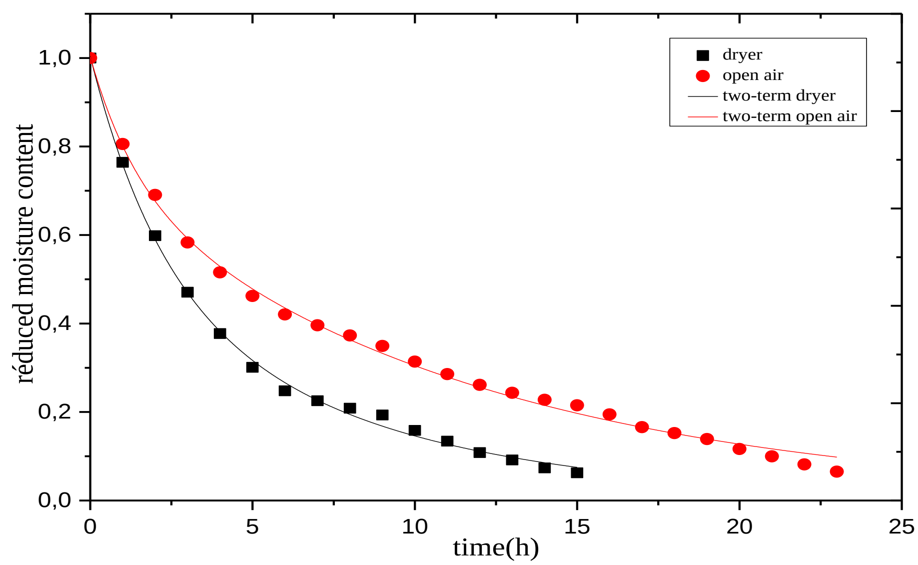


Fig.5: Comparison of the Two-Term Model with Experimental Results

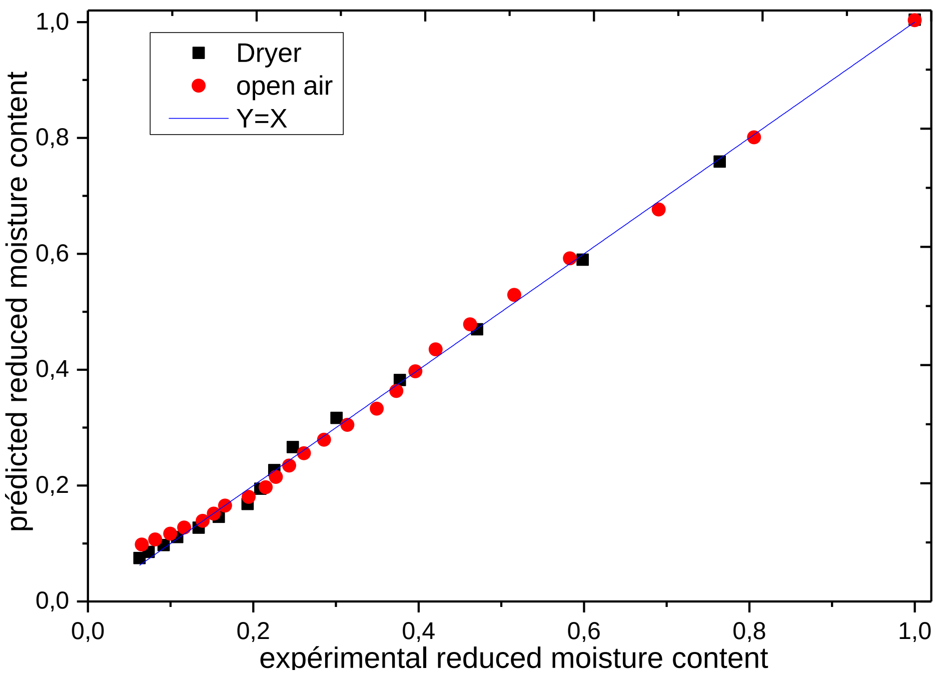


Fig.6: Predicted reduced humidity as a function of experimental reduced humidity

This mathematical model can indeed predict the drying of fish for different drying conditions. The comparison between the predicted relative humidity and that obtained experimentally confirms the agreement of this model as shown in Figure 6. It can be seen that the dashed line from the representation of the predicted values of the two-term model, combined with those obtained experimentally gives the perfect fit line of the straight line (X=Y). Therefore, the Tow-term model could be a good tool to predict fish drying.

Determination of effective diffusivity:

The effective diffusivity of the fish for each type of drying has been shown in Figure 7, which gives the variation of the logarithm of the experimental data of reduced moisture over time. This resulted to a steering coefficient slope of $\left(\frac{\pi^2 D_{eff} t}{L^2}\right)$.

The Deff results for the two drying conditions are shown in Table 3. It shows that the effective diffusivity of the fish ranges from 9.88823 10-7 (m²/s) for open air drying with a mean temperature of 30°C to 1.72534 10-6 (m²/s) for the dryer with an average temperature of 50°C. This result is within the range found by Pranav Mehta et al for fish. These results also show that the diffusivity depends on the drying conditions. The diffusivity is higher in the dryer, showing its dependence to the temperature, as confirmed previously in other works [6,1,22,16].

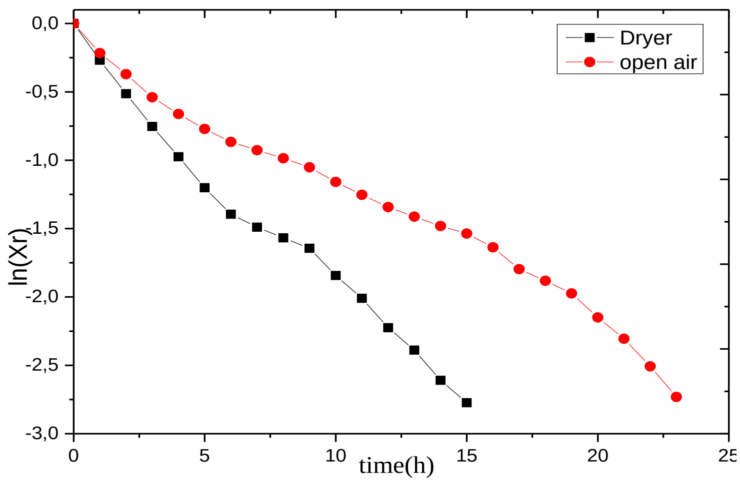


Fig.7: change in logarithm of reduced humidity

Table 3: Diffusivity of the fish for a thickness of 1cm

Conditions	effective diffusivity **(m^2/s)**	**r²**	**RMSE**	**Reduced square χ^2**
open air	1,72534 10^{-6}	0,98615	0,1418	0,00945
dryer	9,88823 10^{-7}	0,97945	0,01072	0,24646

Conclusion:-

In this work, the study of the drying of grey seabream pre-treated with a salt brine was carried out under an average irradiance of 530W/m², an average temperature in the dryer of 50°C and 30°C in the open air. Drying took 15 hours in the dryer and 24 hours in the open air from an initial humidity after pre-treatment of 65% to a final humidity of 32%. The two-term model was chosen as the one that could describe the variation of the reduced humidity of the drying of the grey seabream pre-treated with a salt brine. This model can predict the solar drying of the fish for different drying conditions. The effective diffusivity of the grey seabream found was 9.88825 10-7 for open air drying and 1.72534 10-6 for dryer drying.

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