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MATHEMATICAL MODELLING AND ANALYSIS OF SORPTION ISOTHERMS OF ONIONS (*Allium cepa* L.)

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ABSTRACT

The equilibrium moisture content (EMC) of onion slices was investigated under various drying conditions characterized by different temperatures and relative humidity levels. To identify the most suitable model for representing the experimental data, six EMC models were evaluated. The adsorption isotherms demonstrated a decreasing trend in EMC with increasing temperature at a constant relative humidity. Among the models assessed, the Modified Exponential and Modified Oswin models provided the most accurate predictions of EMC for onion slices. The Modified Exponential model was chosen as the optimal model for drying onion slices due to its superior performance, evidenced by a high coefficient of determination (R^2 = 0.9935) and lower values of error metrics, specifically the reduced chi-square (χ^2 = 0.00038), root mean square error (RMSE = 0.01807), and mean relative deviation modulus (P = 8.26). To further validate these findings, an artificial neural network (ANN) model was implemented in MATLAB, which corroborated the results obtained from the mathematical models. The comparative analysis between the mathematical and ANN models indicated a high degree of agreement with the sorption characteristics of sliced onions.

Keywords: Artificial Neural Network, Drying, Exponential model, Onion slices, Oswin model

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Onion (*Allium cepa* L.) is a globally significant vegetable spice crop belonging to the genus Allium, renowned for its extensive cultivation and consumption worldwide. Used both raw and in processed forms, onion enhances flavour and nutritional value across a wide range of culinary applications. Consequently, the global demand for onions continues to rise. Onions can be processed into various products such as onion paste, dried slices, powder, oil, vinegar, sauce, and pickle (Mitra *et al.*, 2012). Notably, dried onion slices can be converted into onion powder through milling, which exhibits superior rehydration properties compared to dried flakes. This powdered form dissolves rapidly, imparting onion flavour efficiently to diverse food products. To improve the quality of onion products, advancements in drying and storage systems are essential. The structure, surface texture, and shelf-life of dried agricultural products are significantly influenced by their adsorption/desorption characteristics (Attkan *et al.*, 2014). Sorption isotherms serve as a valuable thermodynamic tool to understand the interactions between water and food products. This understanding aids in optimizing food processing operations, including drying, mixing, storage, and packaging. Sorption isotherms can provide insights into structural features such as size, surface area, crystallinity, and volume. Such information is crucial for selecting appropriate storage conditions, packaging methods, and handling systems, which can enhance aroma retention, colour stability, textural attributes, nutritional content, and biological stability of food products (Alam and Singh, 2011; Alam *et al.*, 2018; Debnath *et al.*, 2002; Mehta and Singh, 2006).

Researchers have developed various mathematical, theoretical, and empirical equations to characterize the sorption isotherms of different food products. Numerous models have been proposed to explore the relationship between relative humidity (RH) and equilibrium moisture content (EMC) (Chung and Pfost, 1967; Dhingra, 2003; Kiranoudis *et al.*, 1993; Hossain and Bala, 2000; Soysalan and Oztekin, 2001). Additionally, some studies have incorporated the effect of temperature on EMC (Attkan *et al.*, 2016). For instance, Soysalan and Oztekin (2001) evaluated seven EMC equations for aromatic and medicinal plants, finding that the modified Oswin and modified Halsey models provided the best fit for their experimental data. Similarly, the GAB mathematical model was identified as the most appropriate for describing the sorption data of sesame flour (Menkov and Durakova, 2007). In the case of garlic slices, the modified Henderson model was deemed

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adequate based on F-test evaluations, while the GAB model demonstrated superior results (Madamba *et al.*, 1993). Another study focused on the sorption behavior of onion powder, where the BET equation was used to determine the adsorbed water monomolecular layer. The findings revealed values of 2.09% for freeze-dried, 1.96% for vacuum shelf-dried, and 1.94% for through-flow dried samples (Debnath *et al.*, 2002). Beyond traditional mathematical models, neural network algorithms, such as artificial neural networks (ANNs), have also been employed by researchers for predicting and validating mathematical and numerical models (Goyal and Goyal, 2012).

However, a comprehensive study is necessary to address the substantial packaging and storage needs for fruits and vegetables, particularly those in processed food commodities. This research aims to address this gap by experimentally determining the adsorption isotherms for sliced onions. The study involved fitting the experimental data to various selected models and analyzing the isotherms across different temperatures and relative humidity ranges. The results obtained from these models were subsequently validated using an artificial neural network (ANN) model to ensure accuracy and robustness of the findings.

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MATERIALS AND METHODS

Onions (*Allium cepa* L.), cultivar S-48, were sourced from the farms of Punjab Agricultural University, India. The onions were harvested in the morning and temporarily stored in net bags prior to experimentation. They were then manually peeled and sliced to a thickness of 4 mm using a knife. The equilibrium moisture content (EMC) of the samples was determined using the static desiccator method (Alam and Singh, 2011). An incubator (STXBOD, Stericox® Systems, India) was employed to maintain the desired temperature, while glass desiccators containing glycerol solutions were used to control relative humidity (RH). The humidity levels inside the desiccators were regulated by aqueous glycerol solutions, chosen for their non-toxicity and non-corrosiveness, as opposed to various salts. The glycerol/water solutions were prepared according to the method outlined by Braun and Braun (1958). The relationship between temperature and ERH of glycerol solutions is presented in Table 1. The experimental setup included five RH levels (20%, 40%, 60%, 80%, and 90%) and four different temperatures (15°C, 25°C, 35°C, and 50°C) to standardize the concentration of the glycerol solutions. Temperature and RH within the desiccators were continuously monitored using a digital RH/Temperature data logger (Track-it, Monarch Instruments, USA).

Experimental setup

The aqueous glycerol/water solutions were prepared to the desired concentrations and introduced into the desiccators. After the solutions were added, the desiccators were sealed with lids and allowed to equilibrate for 24 hours to achieve the target relative humidity (RH). Subsequently, 5 grams of sliced onion samples, placed in Petri dishes, were loaded into the desiccators and then transferred to an incubator set to the specified stable temperature. The weight of the samples was recorded at regular intervals until they reached equilibrium. Once equilibrium was achieved, the samples were removed from the desiccators and their final moisture content was determined by drying in a hot air oven at 103°C for 16 hours, as per AOAC (2000) guidelines.

Model validation

The experimental data obtained were analyzed using IBM SPSS 20.0 (Statistical Package for the Social Sciences). The sorption data were then validated against six equilibrium moisture content (EMC) models (Table 2), which are commonly used to describe the sorption behavior of various agricultural products (Kiranoudis *et al.*, 1993; Tsami *et al.*, 1990).

Model fitting

Multiple non-linear regression software packages, including Statistica 10 and the trial version of NLREG 6.6, were employed to fit the experimental data. The

Table 1. Aqueous glycerol concentrations at various temperature and relative humidity

Relative humidity (%)	Temperature (°C)			
	15	25	35	50
	Glycerol concentration (% by weight)			
20	95.71	96.20	96.45	96.33
40	86.42	85.98	86.23	86.54
60	73.57	72.36	72.02	72.26
80	51.20	51.47	50.41	50.96
90	33.24	34.20	35.28	35.02

Table 2. Isotherm models for fitting the experimental data

Sr. No.	Model Name	Equation	References
1	Modified Exponential	$M_e = (A - B * T) * \exp(C * rh)$	[Alam and Singh, 2011; Dhingra, 2003]
2	Modified Halsey	$M_e = \left[\frac{\exp(A - B * T)}{-A * (T + C)}\right]^{\frac{1}{C}}$	[Soysal and Oztekin, 2001; Iglesias and Chirife, 1976]
3	Modified Oswin	$M_e = \left[\frac{A + B * T}{\left(\frac{1}{rh} - 1\right)^{\frac{1}{C}}}\right]$	[Menkov and Dinkov, 1999; Garg and Chandra, 2003]
4	Modified Chung-Pfost	$M_e = \left[\frac{1}{-A}\right] * \ln\left[\frac{(T * B) * \ln(rh)}{-C}\right]$	[Chung and Pfost, 1967]
5	Guggenheim-Anderson-de Boer (GAB)	$M_e = \left[\frac{A * B * C * rh}{(1 - B * rh) * (1 - B * rh + B * C * rh)}\right]$	[Alam and Singh, 2011; Kiranoudis *et al.*, 1993; Madamba *et al.*, 1993]
6	Modified BET	$M_e = \frac{A}{(1 - rh * B)}$	[Hossain and Bala, 2000]

M_e = Equilibrium moisture content (% dry basis), RH = Relative humidity (%), T = temperature (°C), equilibrium coefficient = A, B and C

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equilibrium moisture content (EMC) values predicted by the selected EMC equations (EMC_{fitted}) were calculated for four different temperatures and five different relative humidity (RH) levels. The residuals, defined as the difference between the experimental EMC (EMC_{expt}) and the fitted EMC (EMC_{fitted}), were analyzed to assess the goodness of fit. This assessment involved calculating various statistical parameters, including the coefficient of determination (R^2), reduced chi-square (χ^2), root mean square error (RMSE), and mean relative deviation modulus (P) (Jain and Pathare, 2004), using the formulas provided in equations 1-4.

$$R^2 = 1 - \frac{\text{Residual sum of squares}}{\text{Corrected sum of squares}} \quad \text{.....1}$$

where

$$\text{Residual Sum of Squares} = \sum_{i=1}^{N}(EMC_{expt,i} - EMC_{fitted,i})^2$$

$$\text{Corrected Sum of Squares} = \sum_{i=1}^{N}(EMC_{expt,i} - EMC_{mean,i})^2$$

$$EMC_{mean} = \sum_{i=1}^{N}\frac{EMC_{expt,i}}{N}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(EMC_{expt,i} - EMC_{fitted,i})^2}{N - n} \quad \text{.....2}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(EMC_{expt,i} - EMC_{fitted,i})^2}{N}} \quad \text{.....3}$$

$$P = \frac{100}{n}\sum_{i=1}^{n}\frac{|EMC_{expt,i} - EMC_{mean,i}|}{EMC_{expt,i}} \quad \text{.....4}$$

where

$EMC_{expt,i}$ = i^{th} experimental value,

$EMC_{fitted,i}$ = i^{th} fitted value,

EMC_{mean} = Average of experimental EMC,

N = Number of observations and

n = Number of coefficients.

A model is considered to fit best when the coefficient of determination (R^2) is maximized, ideally approaching unity, and when the reduced chi-square (χ^2) value is minimized. The root mean square error (RMSE) assesses the model's fitting ability relative to the number of data points; a smaller RMSE value, closer to zero, indicates better model performance. Additionally, the mean relative deviation modulus (P) reflects the fit quality, with values less than 5.0 indicating an excellent fit and values greater than 10.0 suggesting a poor fit (Alam and Singh, 2011; Basu *et al.*, 2006).

Artificial Neural Network (ANN)

The artificial neural network (ANN) model is an algebraic framework that emulates the capabilities of biological neural systems to approximate complex relationships. In this study, a multilayer perceptron (MLP) was designed, consisting of two input neurons (representing relative humidity and temperature), one or more hidden layers, and an output neuron representing the equilibrium moisture content (EMC) on a dry basis. The MLP was implemented using the ANN module in MATLAB (version 2019a). Figure 1 illustrates the architecture of the multilayer perceptron. The accuracy of the predictions was enhanced by optimizing the number of neurons in the hidden layers through trial and error. It was determined that a minimum of ten neurons was necessary to construct a robust model, as adding

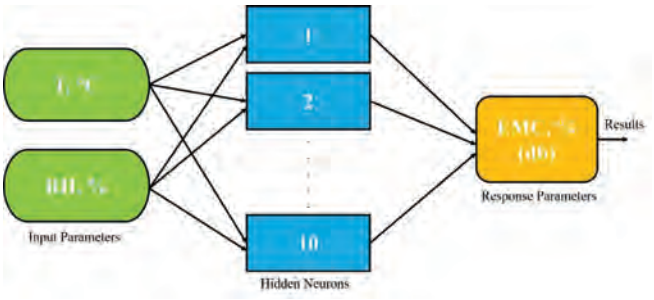


Fig. 1. ANN (Artificial Neural Network) Design

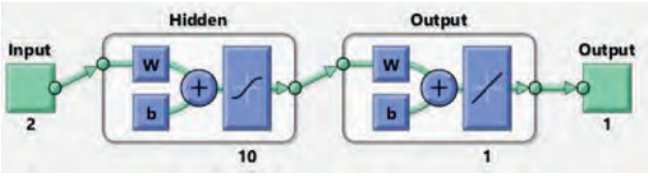


Fig. 2. Modeled Neural Network Process

more neurons could increase the risk of overfitting. To develop the model, 90% of the experimental data were used for training, while the remaining data were divided equally between model validation and testing. The training process involved plotting the input data against the numeric targets to refine the model's fit. As recommended, the majority of the data (14 samples) were used for training the ANN, with 3 samples each allocated for validation and testing, as detailed in Table 5. This approach ensures a comprehensive evaluation of the ANN model's performance.

RESULTS AND DISCUSSION

The equilibrium moisture content (EMC) for onion slices was experimentally determined across a temperature range of 15°C, 25°C, 35°C, and 50°C, and relative humidity (RH) levels of 20%, 40%, 60%, 80%, and 90%. The experimental data are illustrated in Figure 3. Various equations listed in table 2 were applied to the data to identify the best-fitting model. The mean EMC values, based on triplicate measurements for each RH and temperature, are presented in Table 3. The experimentally obtained EMC values for onion slices ranged from 7.2% to 61.51% (on a dry basis), while the fitted EMC values ranged from 7.3% to 60.93% (on a dry basis). It was observed that EMC increased with rising RH at all temperatures and decreased with increasing temperature at a constant RH. This behaviour can be attributed to the rise in vapour pressure of water with increasing temperature, which enhances the rate of water transfer from the agricultural product to the surrounding environment (Hossain and Bala, 2000). Additionally, temperature changes influence water binding and solubility dynamics, further affecting EMC (Alam and Singh, 2011).

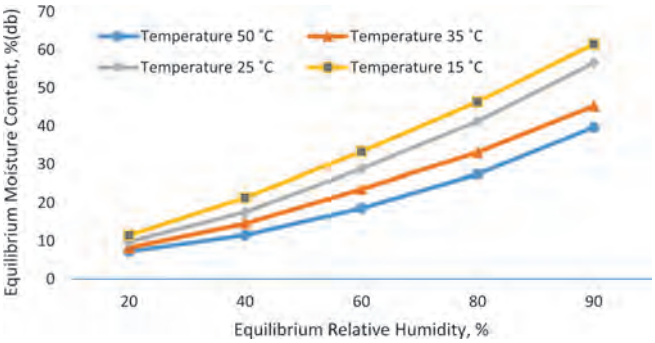


Fig. 3. Experimental sorption isotherms of onion slices for different relative humidities and temperatures

The experimental isotherms obtained in this study were found to resemble those reported for a variety of agricultural products. Similar patterns have been documented for a range of items, including potato, carrot, tomato, green pepper, onion, red chilies, banana, tobacco seeds, medicinal and aromatic plants, and aonla flakes (Alam and Singh, 2011; Hossain and Bala, 2000; Kiranoudis *et al.*, 1993; Menkov and Dinkov, 2007; Mehta and Singh, 2006; Soysal and Oztekin, 2001; Phoungchandang and Woods, 2000).

The relationship between observed and predicted values was found to be significant across the relative humidity range of 20-90% (Table 4). The selected EMC models were fitted to the experimental data, and the results for the best-fitting model, the Modified Exponential model, are summarized in table 3.

To evaluate the performance of the selected EMC models, various statistical parameters and error terms were analyzed, including the coefficient of determination (R^2), reduced chi-square (χ^2), root mean square error (RMSE), and mean relative deviation modulus (P) (Table 4). The Chung-Pfost Modified, Modified Halsey, Modified Oswin, BET, and GAB models were found to be less accurate due to their low R^2 values and high error terms (RMSE, χ^2, and P). In contrast, the Modified Exponential model demonstrated a high R^2 value and low error terms, indicating its superior performance. Figure 4 illustrates the comparison between experimental and predicted EMC values at various temperatures. All models exhibited high R^2 values (>0.90) across different treatments. Notably, the Modified Exponential and Modified Oswin models achieved the highest R^2 values (0.9935 and 0.9929, respectively) and the lowest error terms (RMSE = 0.01807 and 0.01889, P = 8.26 and 27.37, respectively) for onion slices. These findings are consistent with similar observations reported by Alam and Singh (2011).

Figure 5 presents a comparison between the experimental and fitted EMC values predicted by the Modified Exponential model at four different

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Table 3. Mean EMC of onion slices at different temperatures and relative humidity

Temp (°C)	RH (%)	EMC_{expt}	EMC_{expt} (%)	EMC_{fitted}	EMC_{fitted} (%)	Residuals	$(Residuals)^2$	$Abs\left(\frac{Resi}{EMC_{expt}}\right)$
15	20	0.1150	11.50	0.1227	12.27	-0.0077	0.00006	0.0666
15	40	0.2134	21.34	0.1939	19.39	0.0195	0.00038	0.0913
15	60	0.3332	33.32	0.3065	30.65	0.0267	0.00071	0.0800
15	80	0.4632	46.32	0.4846	48.46	-0.0214	0.00046	0.0462
15	90	0.6151	61.51	0.6093	60.93	0.0058	0.00003	0.0095
25	20	0.0980	9.80	0.1085	10.85	-0.0105	0.00011	0.1069
25	40	0.1760	17.60	0.1715	17.15	0.0045	0.00002	0.0256
25	60	0.2882	28.82	0.2711	27.11	0.0171	0.00029	0.0594
25	80	0.4123	41.23	0.4286	42.86	-0.0163	0.00026	0.0394
25	90	0.5657	56.57	0.5389	53.89	0.0269	0.00072	0.0475
35	20	0.0820	8.20	0.0943	09.43	-0.0123	0.00015	0.1499
35	40	0.1456	14.56	0.1491	14.91	-0.0035	0.00001	0.0238
35	60	0.2355	23.55	0.2356	23.56	-0.0001	0.00000	0.0006
35	80	0.3312	33.12	0.3725	37.25	-0.0413	0.00171	0.1247
35	90	0.4523	45.23	0.4684	46.84	-0.0161	0.00026	0.0355
50	20	0.0720	7.20	0.0730	7.30	-0.0010	0.00001	0.0142
50	40	0.1150	11.50	0.1154	11.54	-0.0004	0.00001	0.0037
50	60	0.1856	18.56	0.1825	18.25	0.0031	0.00001	0.0168
50	80	0.2743	27.43	0.2885	28.85	-0.0142	0.00020	0.0516
50	90	0.3965	39.65	0.3627	36.27	0.0338	0.00114	0.0853
						Sum	0.2478	1.0787
						RMSE	0.01807	
						χ^2	**0.00038**	
						r^2	0.9935	
						P	8.26	

Table 4. Estimated values and comparison criteria of EMC models

Coefficients	Equations					
	Modified Exponential	Modified Halsey	Modified Oswin	Modified Chung-Pfost	GAB	BET
A	0.09105	-2.66820	0.29200	6.58820	0.15651	0.10916
B	0.00090	0.02857	-0.00290	7.45296	0.78875	0.87490
C	2.28973	1.95013	2.35558	102.0820	5.54745	-
Comparison criteria						
R^2	0.9935	0.9862	0.9929	0.99163	0.9267	0.9168
RMSE	0.01807	0.02639	0.01889	0.02789	0.05988	0.06362
χ^2	0.00038	0.00082	0.00042	0.00092	0.00429	0.00476
P	8.26	44.77	27.37	13.83	30.23	75.78

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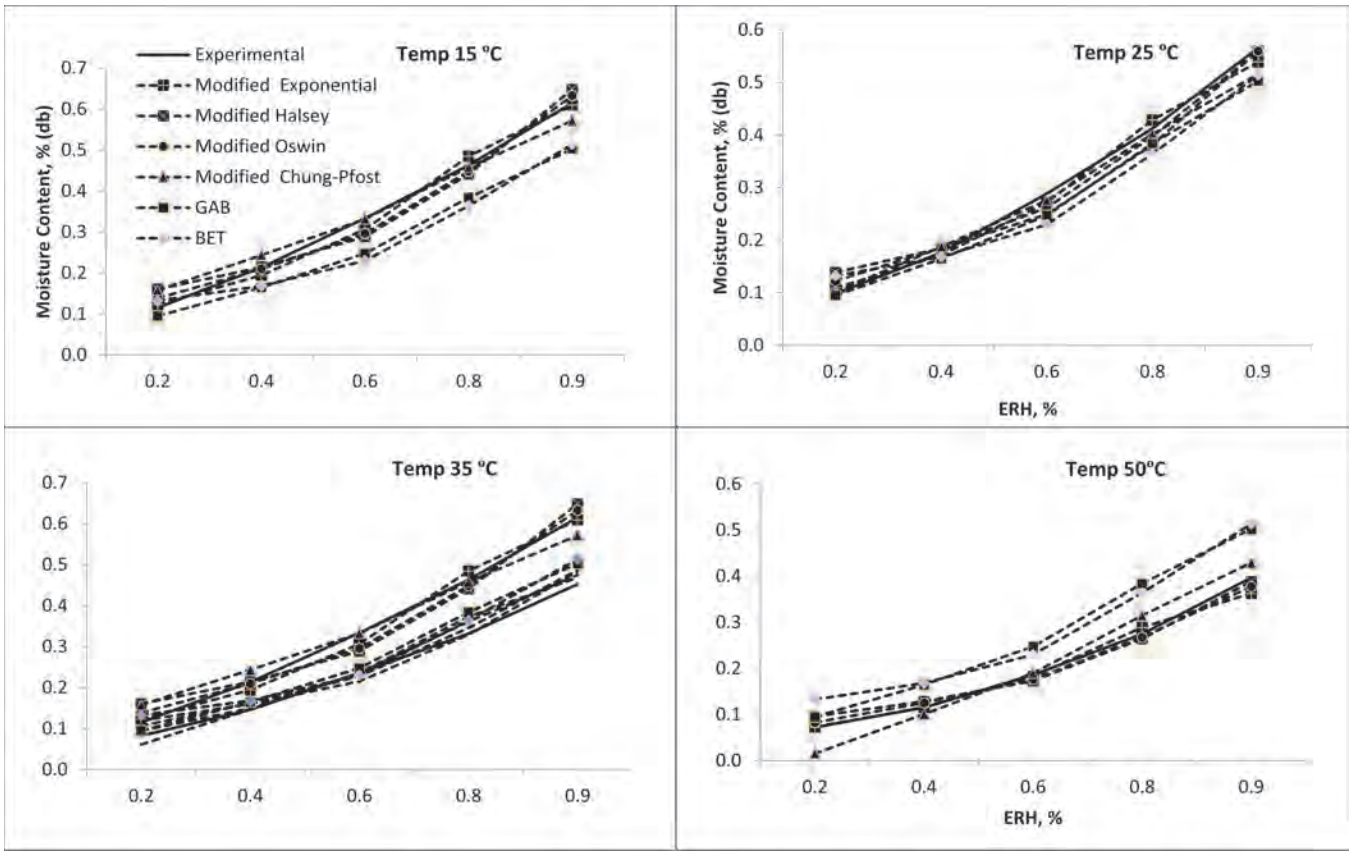


Fig. 4. Comparison of experimental and predicted values for selected models

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temperatures. The analysis reveals that the experimental data closely align with the predicted values of the Modified Exponential model, demonstrating its effectiveness in accurately describing the sorption behaviour of onion slices. The results of this sorption study indicate that the Modified Exponential model is the most suitable for characterizing the EMC–ERH relationship in onion slices. This finding aligns with similar results reported for red chilies, where the Modified Smith model was identified as the best fit out of seven evaluated EMC models (Hossain and Bala, 2000). Additionally, in a study on tomato drying, the Modified Henderson and Modified Halsey models were recommended for their accuracy (Viswanathan *et al.*, 2003).

ANN Modeling

The neural network model is fundamentally based on technical models that simulate neural structures. It consists of neurons organized into layers, including input parameters, hidden neurons, and output responses. As illustrated in Figure 6, this approach has led to the development of a sophisticated and versatile model. It can be adjusted to evaluate various mappings by optimizing the number of layers and neurons to achieve the desired level of sensitivity and accuracy.

Table 5 presents the results obtained from the neural network model evaluation. The Mean Square Error (MSE) measures the average squared difference between the predicted responses and the actual targets. A lower MSE indicates minimal error, with a value of zero representing perfect accuracy. The regression (R) values reflect the strength of the relationship between the predicted responses and the actual targets, with an R-value of 1 indicating a perfect correlation and an R-value of 0 indicating no correlation. In this study,

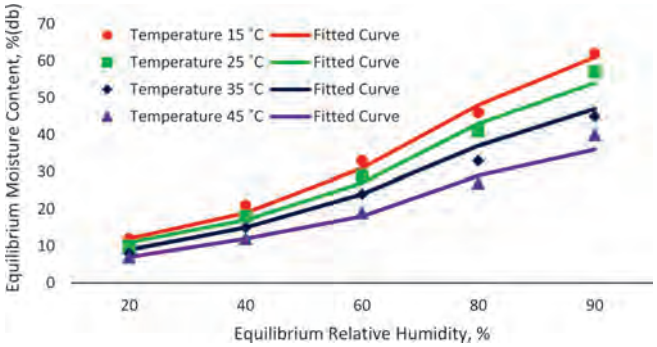


Fig. 5. Comparison of the experimental and fitted values of EMC using modified Exponential model at different temperatures

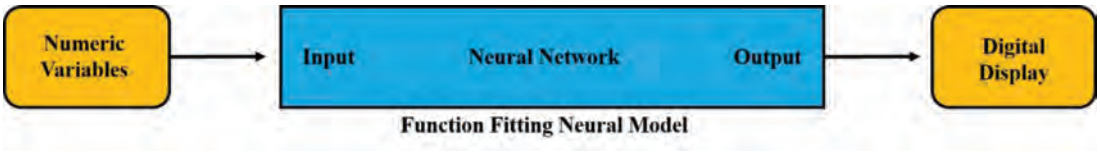


Fig. 6. Neural Network Model

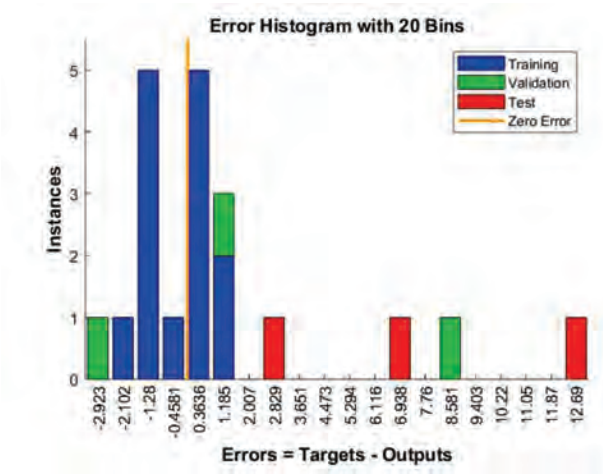


Fig. 7. Error Histogram Chart

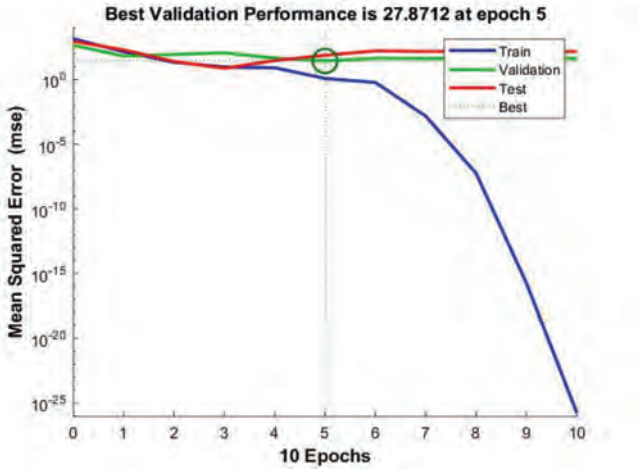


Fig. 8. Performance Curve

Table 5. Mean Squared Error and R values from model

	Sample	MSE	R
Training	14	1.21746e-0	9.97799e-1
Validation	3	27.8711e-0	9.96104e-1
Testing	3	75.17454e-0	8.83336e-1

the ANN achieved MSE values close to zero and an R-value close to one, demonstrating highly accurate curve fitting. The error histogram for the optimized neural network model is shown in Figure 7, illustrating the distribution of errors and further supporting the model's precision.

The neural network model was meticulously designed and its performance evaluated to determine if any adjustments were necessary during the training process. Figure 8 illustrates the performance curve of the developed models, with the optimal validation performance occurring at the fifth iteration. The regression plots for testing, training, and validation are shown in Figure 9, highlighting the relationship between the target and the model's responses. The results indicate that both validation and test outcomes achieved R-values greater than 0.90, demonstrating a strong correlation. Figure 8 also indicates that the best validation performance was achieved at 27.87°C. Consequently, a comparative analysis of the Modified Exponential Model (MEM), the artificial neural network (ANN), and experimental values was conducted using the conditions of 35°C and 20% RH from Table 3. The

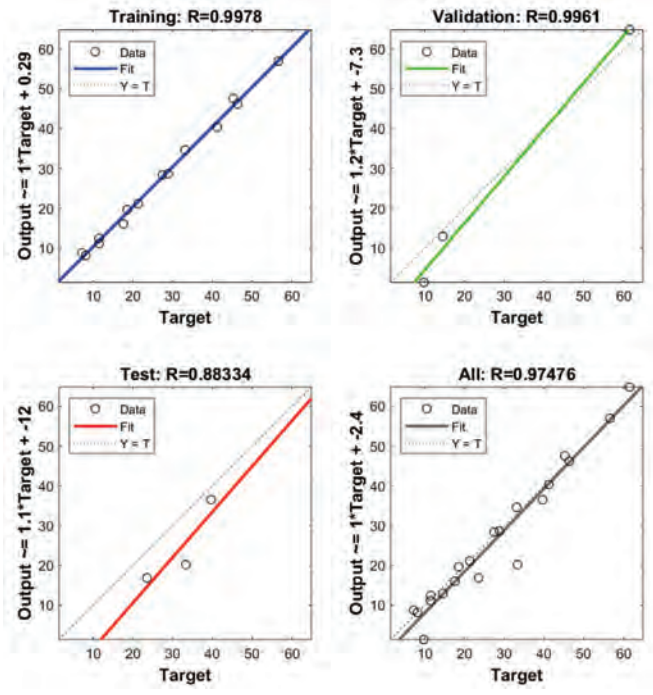


Fig. 9. Regression Curve

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results showed a deviation of 0.146% from the MEM values (Table 6). These findings reflect an exceptional agreement between the predictions made by the neural network and the validation standards, highlighting the model's accuracy and reliability.

Table 6. Comparative Analysis of ANN* and MEM**

Parametric values	EMC_{MEM**}	EMC_{ANN*}	Deviation
T,°C : 35; RH, %: 20	8.200	8.212	0.146%

*Artificial Neural Network, **Modified Exponential Model, T = Temperature, RH = Relative humidity

CONCLUSION

The equilibrium moisture content (EMC)–relative humidity (ERH) relationship for onion slices was most accurately predicted by the Modified Exponential model within the relative humidity range of 20-90%. This model was preferred due to its high coefficient of determination (R^2 = 0.9935) and low error terms, including a root mean square error (RMSE) of 0.01807, a reduced chi-square (χ^2) of 0.00038, and a mean relative deviation modulus (P) of 8.26, when compared to five other EMC models. Consequently, the Modified Exponential model is recommended for predicting the adsorption isotherms of sliced onions. MATLAB was employed to develop a highly effective neural network model, which delivered exceptional results with multiple hidden layers and neurons. The optimal network configuration included ten hidden layers and demonstrated a deviation of only 0.146% in EMC compared to the results from the Modified Exponential model. The findings from this study affirm that artificial neural network (ANN) models are highly effective for validating sorption isotherms for sliced onions, showcasing their potential for accurate and reliable predictions.

Authors contribution

Conceptualization and designing of the research work (AKA, MSA); Execution of field/lab experiments and data collection (AKA, AR); Data analysis and interpretation (AKA, SK, PA); Manuscript preparation (AKA).

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