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Designing the Thermal Process for Sterilizing Canned Fish in the Autoclave: Modeling Temperatures with Artificial Neural Networks, Thermal Penetration Characteristics and Predicting Shelf Life

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ABSTRACT

The current study aimed to sterilize canned fish cans using an autoclave, as well as addressing the thermal penetration characteristics and predicting shelf life. Thermal penetration characteristics were study, along with the calculation of their thermal process, and the application of artificial intelligence (ANN) was used to predict the sterilizer and cold spot temperature, as well as the lethal rate. The cold spot in the cans and the lethal rate during storage were investigated. The autoclave was used to sterilize the fish at two temperatures, 110 and 121°C, with a holding time of 20min. The results showed that the come-up time (CUT) for the sterilizer to reach the sterilization temperature at 110°C was 32min, while at 121°C temperature, it required 36min. The lethal rate at a temperature of 121°C reached 1 after 44min of heating, while at a temperature of 110°C, it reached 1 after 40min. The results showed that the fitting between the experimental sterilizer temperature, the cold spot in the cans, and the predicted lethal rate by ANN was good. Moreover, the MSE value was very low, ranging between 6.4152×10^{-7} and 0.0034599. The general model Sin 4-8 equations were used to describe the sterilizer temperature, the cold spot in the cans, and the lethal rate, respectively. The results showed that the thermal penetration coefficient (f_h) was 15.01 and 28.57 at temperatures of 110 and 121°C, respectively. The TBA value in sterilized canned fish at temperatures of 110 and 121ºC was 0.11 and 0.16, respectively. The predicted shelf life was 15.83 and 18.64 months at temperatures of 110 and 121°C, respectively.

INTRODUCTION

The application of high temperatures is one of the most common methods for eliminating or controlling the number of microorganisms present in foods and on packaging surfaces. The importance of these treatments in the food industry can be seen through the reduction in food storage spaces, especially on shelves, as well as preservation at different temperature levels. **Al-Rubaiy *et al.* (2020)** have preserved fish using infrared drying as a heat treatment medium to eliminate microorganisms. Through studies and the efforts of food producers to find more reliable ways to produce high-

quality canned foods, many attempts have been made to introduce food products manufactured with new technologies such as ultra-high pressure and pulsed electric fields into grocery markets. However, the significance of this type of food remains relatively small compared to thermal treatments **(Tadini & Gut, 2022)**.

Dornoush and Bagher (2022) mentioned that the thermal treatment is a general term that describes all forms of thermal treatments in which the numbers of microorganisms and spoilage agents are controlled. This includes types of heat-treated containers such as metal and glass containers **(Ababouch, 2002)**. Thermal treatment has been used to achieve long-term storage stability for a wide range of products, especially seafood, which is one of the most widely used methods for preserving fish. These treatments aim to produce a safe, high-quality fish product at prices affordable to consumers. The idea of canning and thermal treatments began with the advancement of the industrial revolution **(Azizi-Lalabadi *et al.*, 2023)**. The success of thermal sterilization requires balancing the beneficial effects of thermal treatments with the preservation of the qualitative properties of foods. Some desirable changes in food may occur during thermal treatment by eliminating spoilage agents from microorganisms and their enzymes, as well as the internal enzymes of the food material. However, some changes are undesirable, such as the hardness and darkening of canned fish surfaces and other packaged products due to contact with the hot inner surface of the can **(Stumbo, 1973)**. The term "thermal treatments" is associated with thermophilic microorganisms, as the strategy of thermal killing can be summarized by eliminating or reducing microbial and enzymatic activity thermally with the aim of prolonging the shelf life of the product without affecting consumer health. This strategy cannot be applied without a complete understanding of the thermal resistance of microorganisms **(Peleg *et al.*, 2005)**. **Chandan (2015)** and **Nagarajarao (2016)** mentioned that sterilization is a process in which food is heated at high temperatures for a specific period to kill their microbial cells and spores, as well as inhibiting enzymes. As a result, canned and sterilized foods have a long shelf life at ambient temperatures. In addition, these foods are also cooked and therefore require minimal heating before consumption. However, severe heat treatment during the sterilization process may result in significant changes in the qualitative properties of the food. **Toledo (2007)**, **Holdsworth and Simpson (2016)** and **Zhang *et al.* (2018)** indicated that the thermal resistance value Z is a unique parameter for describing the thermal resistance of pathogenic microbes, which is the increase in temperature necessary to perform a complete thermal sterilization process to prevent microbial growth in the food product. In low-acid foods, Clostridium bacteria are the most heat-resistant pathogens that may survive the thermal process, leading to the germination of their spores in the absence of oxygen, producing a potent toxin that can cause death within days. This type is referred to as botulism **(Tucker & Featherstone, 2021)**.

ANNs, consisting of output, hidden, and input layers, are stable, effective, and unique in explaining nonlinear relationships between variables, making them commonly used in

complex systems **(Talib *et al.*, 2019)**. ANNs, essentially black boxes, use multiple input variables to predict output variables without prior knowledge. They're popular in agriculture and engineering and are essential for modern technology advancements. With industrial automation and the Internet of Things, ANNs make data gathering and monitoring more accessible **(Ngankham *et al.*, 2011, Tohido *et al.*, 2012; Nayak *et al.*, 2020)**. Artificial neural networks (ANNs) in food science aid in problem-solving, design improvements, and machine learning design limitations, originating from AI research focusing on proper training methods and data **(Talib *et al.*, 2019; Khadir 2021)**. The current study aimed to conduct the canning and sterilization of the Talang queenfish (*Scomberoides commersonianus*) using the autoclave device model and the species thermal properties with artificial neural networks, as well as examining the value of thiobarbituric acid and pH during storage periods and predicting the shelf life.

MATERIALS AND METHODS

Raw materials

Talang queenfish (*Scomberoides commersonianus*) was purchased from the local fish market in Basrah Governorate in Iraq. It was placed in a polystyrene box containing crushed ice. The fish were cleaned by removing the head, internal organs, gills, tail, and fins, then thoroughly washed with tap water until all blood residues were completely removed. The cleaned fish were cut into fillets and stored at a temperature of -18°C until the canning process was carried out. A 370mL glass jars were used for canning fish.

Primary heat treatment

The sliced fish samples were placed in a stainless-steel pot, and 2500mL of reverse osmosis water was added. The pot was heated to 80ºC for five minutes. Afterward, the fish slices were removed from the pot and placed inside pre-sterilized glass containers. A hot saline solution with a concentration of 2% was added, leaving a headspace in the container, and the containers were sealed tightly for sterilization.

Autoclave sterilization process

The FANEM autoclave was used to sterilize the canned fish. The temperature inside the autoclave and the cold spot in the cans were measured. After reaching the required temperature, the cans were left for 20min at 110 and 121ºC. Then, the autoclave was turned off, and the glass cans were cooled with tap water. Afterward, the glass cans were stored at room temperature for testing purposes.

Calculating the thermal process for sterilizing fish cans

The duration of the thermal process was calculated using the Ball method from the following equation:

$$B = f_h log\left[\frac{j_{Ch}\ I_h}{g}\right] \quad (1)$$

The value of, I_h was calculated for the heating process by the following equation:

$$I_h = (T_R - T_{ih}) \quad (2)$$

The thermal lag, J_{Ch}, was calculated using the following equation:

$$j_{Ch} = \frac{(T_R - T_{pih})}{(T_R - T_{ih})} \quad (3)$$

Where:

B: Represents the thermal process time, T_{pih}.: The initial delusion heating temperature, T_R: The sterilizer temperature, T_P: The product temperature, T_{ih}: The temperature at the beginning of the heating process, f_h: Heating rate. In the case of cooling, it is called the cooling rate and is denoted by the symbol f_c. it is the slope of the straight line drawn between the logarithm of temperature and time, and it is defined as the time in minutes required for the thermal penetration curve to pass through one logarithmic cycle.

Decimal reduction time

It is the time required to kill 90% of the microbes during one logarithmic cycle and was calculated using the following equation:

$$D = \frac{t_2 - t_1}{\log(a) - \log\ (b)} \quad (4)$$

Where, t represents time, a represents the number of microorganisms before treatment, b represents the number of microorganisms after treatment, and D represents the decimal reduction time (min).

The thermal resistance constant Z was calculated from equation (5) and is defined as a unique parameter to describe the thermal resistance of bacterial spores, which is the increase in temperature necessary to reduce the value of D by 90%.

$$Z = \frac{T_2 - T_1}{\log(D_1) - \log\ (D_2)} \quad (5)$$

Where, D_1 represents the decimal reduction time when treated at a temperature lower than the required sterilization temperature; D_2 represent the decimal reduction time at the required sterilization temperature; T_1-T_2 represents the difference in temperatures.

The U value was calculated using the following equation:

$$U = F_o\, F_i \tag{6}$$

F_i: the time for the destruction of microorganisms at any other temperature, which was calculated from the following equation:

$$F_i = 10^{(121.1-T_r)/Z} \tag{7}$$

F_o: the time in minutes at the source temperature, which is the temperature at which the vegetative cells and spores begin to be damaged. It was calculated using the following equation:

$$F_o = \sum_{0}^{t} L\, \Delta t \tag{8}$$

$$L = 10^{(T-121.1)/Z} \tag{9}$$

log g is derived from the table of log gg versus fh/U (**Stumbo, 1973)**. The total sterilization time was calculated using the following equation:

$$\mathrm{B}_t = \mathrm{B} + 0.42\ CUT \tag{10}$$

B_t: It is the total sterilization time; B: Time of the process in which thermal death occurs; CUT: represents the time it takes for the sterilizer to reach the required thermal degree (sterilization temperature). The thermal death time can be found by rearranging equation (10):

$$\mathrm{B} = \mathrm{B}_t - 0.42\ CUT \tag{11}$$

pH measurement

5 grams of the sample were mixed with 10ml of distilled water and thoroughly mixed for 2 minutes, then the mixture was filtered, and the pH was measured **(Ismail & Nielsen, 2024)**.

TBA

TBA was calculated following the method indicated by **Ismail and Nielsen (2024)**. 10g of the sample were weighed and mixed with 50mL of distilled water for 2min, then 47.3mL of distilled water was added, and 3.5mL of 4N HCl was added to reduce the pH to 1.5. Glass beads were added to prevent foaming. The mixture was placed in the distillation apparatus, and the contents were heated to collect 50mL of the distilled liquid over 10min. A 5mL of the distilled liquid was taken in a test tube, and 5mL of the previously prepared TBA (0.2883g/ 100mL of 90% glacial acetic acid) was added, and the tube was sealed tightly. The control sample was prepared by placing 5mL of distilled water with 5mL of the reagent, and the tubes were sealed tightly. The tubes were placed in a boiling water bath for 35min, then cooled for 10min. The absorbance was measured at a wavelength of 538 nanometers, according to the TBA number as follows:

TBA (mg malonaldehyde/kg fish) = 7.8D

Total bacterial count

The culture medium nutrient agar (NA) was prepared by dissolving 28g in a liter of distilled water, sterilized, and left until poured into plates. The plates were inoculated from the prepared tubes by transferring 1mL of the dilutions to the plates, then pouring the culture medium and allowing it to solidify. The plates were then incubated at 37°C for 24-48h. This test was conducted for fresh and canned fish thickness during different storage periods **(Pommerville, 2022)**.

Modeling with artificial intelligence

MATLAB's artificial neural network fitting (R2014a, MathWorks Inc., USA) was used to model experimental data generated by ANNs during canned fish sterilization using an autoclave. Multilayer perception included the feedforward backpropagation of the algorithm input layer (heating time in case of autoclave temperature prediction, heating time in case of product temperature prediction, heating time in case of Lethal rate prediction, and storage times in case TBA prediction). In the neural network, ten hidden layers for training on data, and an output layer (case 1: autoclave temperature (Fig. 1a), case 2: product temperature (Fig. 1b), case 3: Lethal rate (Fig. 1c), case 4: TBA (Fig.1d)). The performance function was mean square error (MSE), the adaptation learning function was LEARINGDM, and the training function was TRAUNLM. Ten neurons were employed, along with two layers and the TANSIG transfer function, which was utilized between the input and hidden layers as well as between the hidden layer and the output layer. The ANN models were trained to minimize the error between the experimental and predicted response values. The dataset was trained using the Levenberg–Marquardt algorithm. The weights and bias combined made up the neural network parameters. To

build the ANN model, the experimental data were divided into three groups: 70% for training, 15% for testing, and 15% for validation. The coefficient of correlation was used to assess the performance of the produced ANN model. The following equations were used to get the correlation coefficient (Equation 12) and MSE (Equations 13). MSE were calculated from the following equations:

$$R = \left[\frac{\sum_{i=1}^{n}(y_p - \overline{y_p})^2}{\sum_{i=1}^{n}(y_e - \overline{y_e})^2}\right]^{0.5} \qquad (12)$$

$$MSE = \frac{\sum_{i=1}^{n}(y_p - y_e)^2}{n} \qquad (13)$$

Where, R is the coefficient of correlation; y_p is the predicted data; y_e is the experimental data; MSE is the mean square error; n is the observation number.

Statistical analysis

The SPSS program ver. 21 was used to analyze the experimental data, and LSD at the 0.05 level was used to compare the means of the treatments.

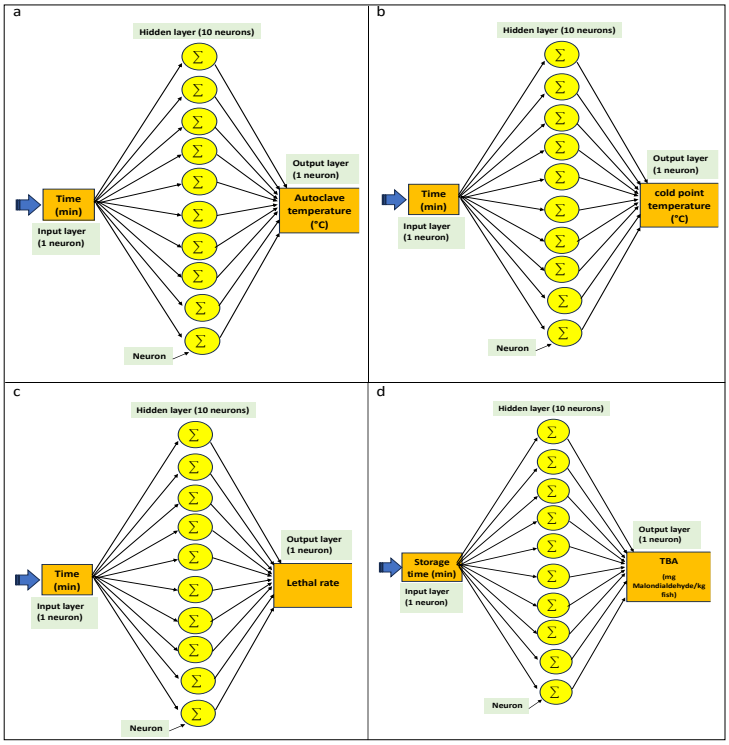

Fig. 1. The feedforward neural network with multilayers: (a) Prediction of autoclave temperature, (b) cold point temperature, (c) Lethal rate, and (d) TBA

RESULTS AND DISCUSSION

It was observed from Fig. (2) that both the sterilizer temperature and the cold spot in the fish cans increased with the heating time. When the time increased from 0-32min, the temperature in the sterilizer increased from 42.84-100°C. The heating process occurred due to the transfer of thermal energy from the electric heater to the water, which raised its temperature. When the time increased from 0-36min, the temperature in the sterilizer rose from 39.02-121°C. It also increased from 29.70 -109.01°C in the fish cans when the heating time was increased from 0-34min. The reason for the rising temperature of the cans was due to the transfer of heat from the hot steam to the surface of the cans by convection, and then the transfer of heat from the walls of the cans to the food inside the cans by conduction. Additionally, when the heating time was increased from 0-42min, the temperature of the cans rose from 32.37- 120.63°C.

As shown in Fig. (2), the time required to reach the sterilization temperature (come-up time (CUT)) in the sterilizer at 110°C was 32min, while at 121°C it took 36min. This is due to the higher sterilization temperature. The holding time at the sterilization temperature of 110 and 121°C was 20min. After that, the temperature of the cans and the sterilizer decreased due to the cooling process with tap water, reaching 30.47 and 30.92°C respectively at a temperature of 110°C. However, at a temperature of 121°C, it decreased to 34.28 and 29.40°C. respectively. Regarding the mortality rate, the results showed that the mortality rate at a temperature of 121ºC began to increase after 30min of heating, reaching 2.53×10^{-2}, and reached 1 after 44min of heating. Meanwhile, at a temperature of 110ºC, it began to increase at 26min, reaching 1.7×10^{-2}, and increased to 1 at 40min. This indicates that all microorganisms in the cans were eliminated.

The results showed that the agreement between the experimental values and those predicted by ANNs was good, with the coefficient of determination being greater than 0.998 (Figs. 3, 5). The MSE values ranged between 0.0034599 and 6.4152×10^{-7} (Figs. 4, 6).

The following equation was to predict the sterilizer temperature at 110ºC, where the statistical indicators of the equation were R-square: 0.9991, SSE= 34.88, Adjusted R-square: 0.9987, RMSE: 1.061:

$$T_{R110}= 79.74\sin(0.00486t_s+1.73) +41.92\sin(0.06202t_s-0.896) +1.035\sin(0.2472t_s+0.326)+7.046\sin(0.1685t_s-1.66) \quad (14)$$

The following equation was used to predict the sterilizer temperature at 121ºC, where the statistical indicators of the equation are R-square: 0.9991, SSE= 41.88, Adjusted R-square: 0.9983, RMSE: 1.245:

T_{R121}=110.1sin (0.02396t_s+ 0.4907) +18.88 sin (0.09569 t_s -2.793) + 9.421sin (0.1096 t_s+5.614) + 3.338sin (0.1943 t_s+ 4.862) + 1.634 sin (0.4955 t_s + 1.153) + 1.042 sin (0.3219 t_s + 4.003) + 1.63 sin (0.4061 t_s + 4.988) + 0.8541 sin (0.6986 t_s + 1.477) (15)

The following equation was to predict the cold point temperature in the cans at 110m, where the statistical indicators of the equation were R-square: 0.9984, SSE= 62.01, Adjusted R-square: 0.9969, RMSE: 1.679:

T_{CP110}= 147.2sin (0.04396 t_s -0.388) + 43.46sin (0.07467 t_s + 1.313) + 22.93sin (0.1617 t_s + 0.4593) + 63.39sin (0.2266 t_s + 0.7754) + 25.75sin (0.276 t_s + 4.832) + 71.56 sin (0.2479t_s+2.965)+1.197sin(0.5013t_s+2.831) (16)

The following equation was used to predict the cold spot temperature in cans at 121ºC, where the statistical indicators of the equation are R-square: 0.9991, SSE= 34.88, Adjusted R-square: 0.9987, RMSE: 1.061:

T_{CP121}=114sin(0.0272t_s+0.2137)+2.196sin(0.05662t_s+0.5733)+ 7.877 sin(0.1197t_s+2.659) + 1.559 sin(0.2417t_s+2.781) +1.028sin(0.3659t_s+1.506) +1.177sin(0.1416t_s+6.555) +0.3609sin(0.3099t_s+3.095)+0.4212sin(0.4743t_s+1.697) (17)

The following equation was used to predict the mortality rate at 110ºC, where the statistical indicators of the equation are R-square: 0.988, SSE= 0.08694, Adjusted R-square: 0.9799, RMSE: 0.05897:

T_{Lr110}=0.3752sin(0.004658t_s+2.049)+0.6843sin (0.1913 t_s -0.543)+0.5701sin (0.08155t_s - 2.129) +0.1062sin(0.3767t_s+0.6458)+0.4373sin (0.2018t_s -4.034) + 0.04805sin (0.5922t_s+ 0.758) (18)

The following equation was used to predict the mortality rate at 121 ºC, where the statistical indicators of the equation were R-square: 0.971, SSE= 0.1699, Adjusted R-square: 0.9463, RMSE: 0.07932:

T_{Lr121}= 0.573 sin (1.454 t_s + 1.629) + 0.601sin (4.644 t_s + 2.006) + 0.07806sin (1.544 t_s + 4.182) +0.484sin(5.604t_s+5.213) +0.4257sin(6.506t_s+2.141) +0.0764sin(9.785t_s+2.184) + 0.04993sin (18.73 t_s -0.01641) + 0.05375sin (16.02 t_s -0.01492) (19)

Thermal penetration characteristics

Fig. (3) shows the heating and cooling curves during sterilization at temperatures of 110 and 121°C while sterilizing fish cans. The relationship between log (T_r-T_p) and

heating time was plotted to obtain the values of f_h and J_h (Fig. 3a, b), moreover to find Jc (Fig. 3c, d) from the plot of the relationship between log (T_r-T_w) and cooling time. All the relationships were represented by a straight line, as shown in the Fig. (3).

It was observed from Table (1), which shows the parameters of the sterilization process at temperatures of 110 and 121°C, that the results indicated a thermal penetration coefficient (f_h) value of 15.01 and 28.57 at temperatures of 110 and 121°C, respectively. The values of fc were 23.25 and 57.8, respectively. The thermal lag coefficient Jc during heating at temperatures of 110 and 121°C were 1.44 and 1.27, respectively. Jc reached 1.45 and 1.1, respectively. As observed from the Table, the total sterilization time B_t was 51.11 and 47.30min. As for the sterilization time B, it reached 37.67, and 30.50min. Whereas the sterilization time at 121°C required less time than at 110°C, this is because the thermal kill process at 121°C is more effective than at 110°C. Fig. (7) shows the coefficients of determination between the experimental and predicted values for autoclave temperature, cold spot in cans, and lethal rate, with the values being very high (greater than 0.90).

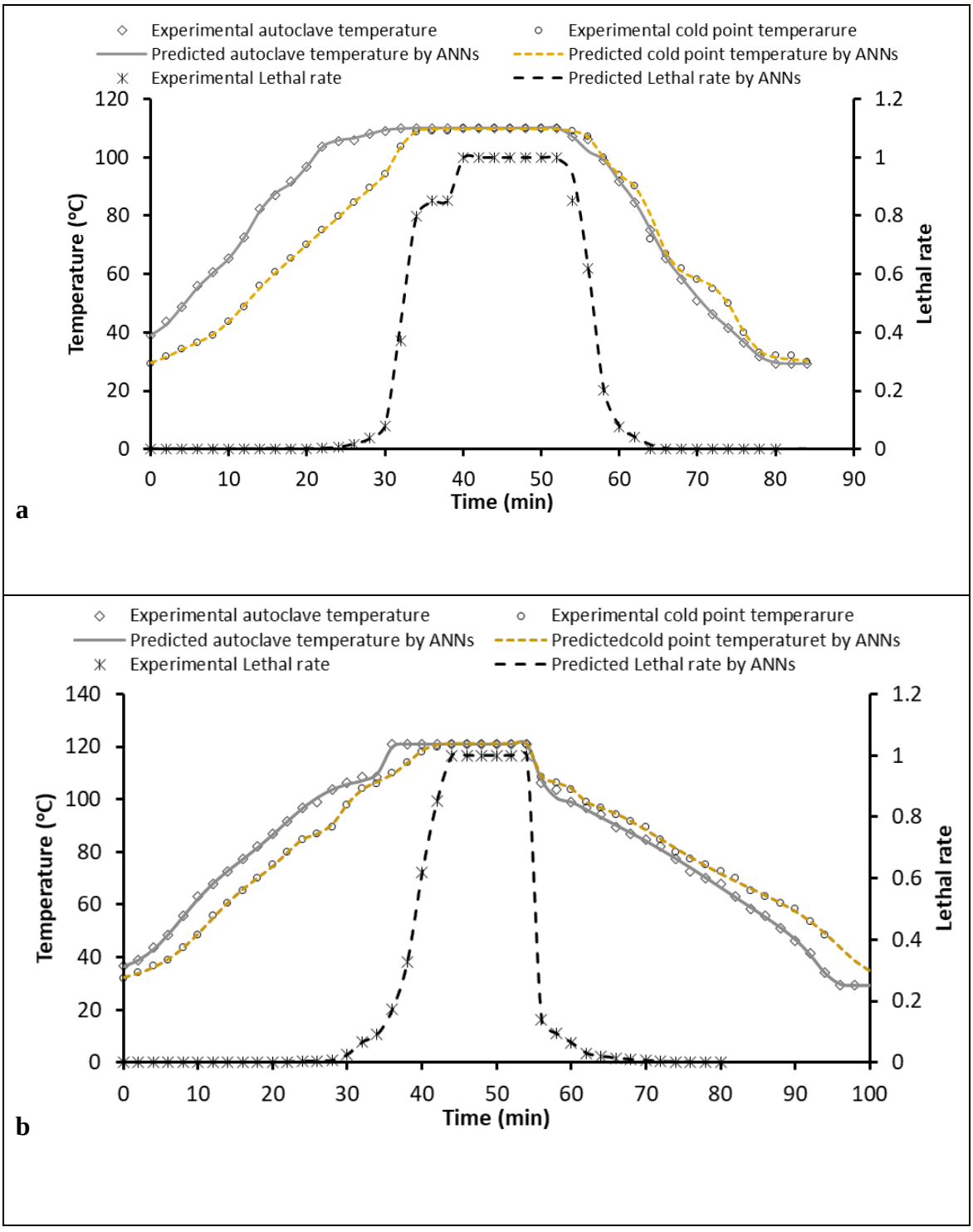

Fig. 2. Experimental and predicted of heat penetration curve of sterilized canned fish by autoclave at temperature of a: 110 °C, and b: 121°C

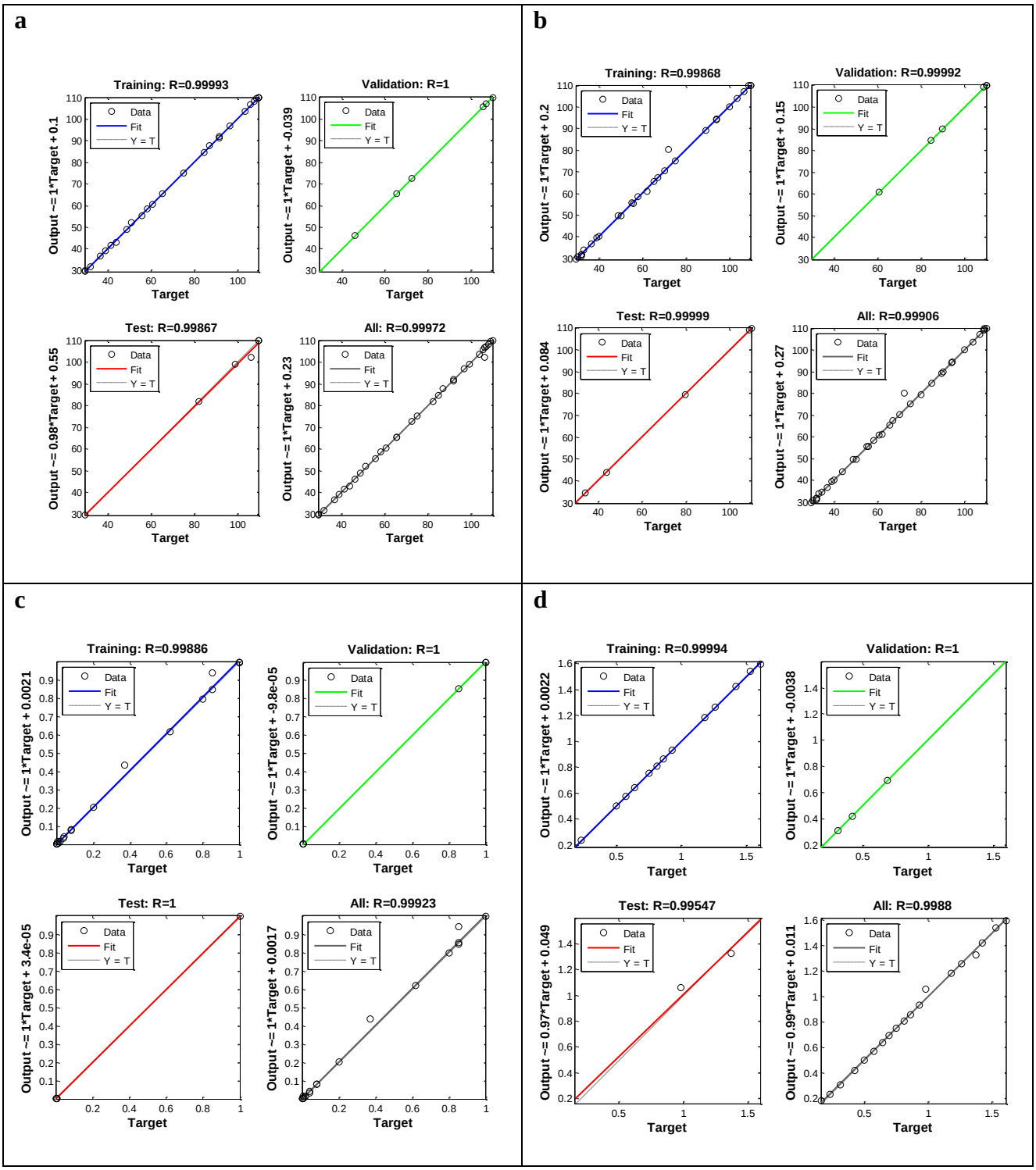

Fig. 3. ANN performance at 110 °C temperature via correlation coefficients (R). autoclave temperature (a), cold point temperature (b), lethal rate (d) for training, validation, test, and all, the target is the experimental and the output is the predicted data

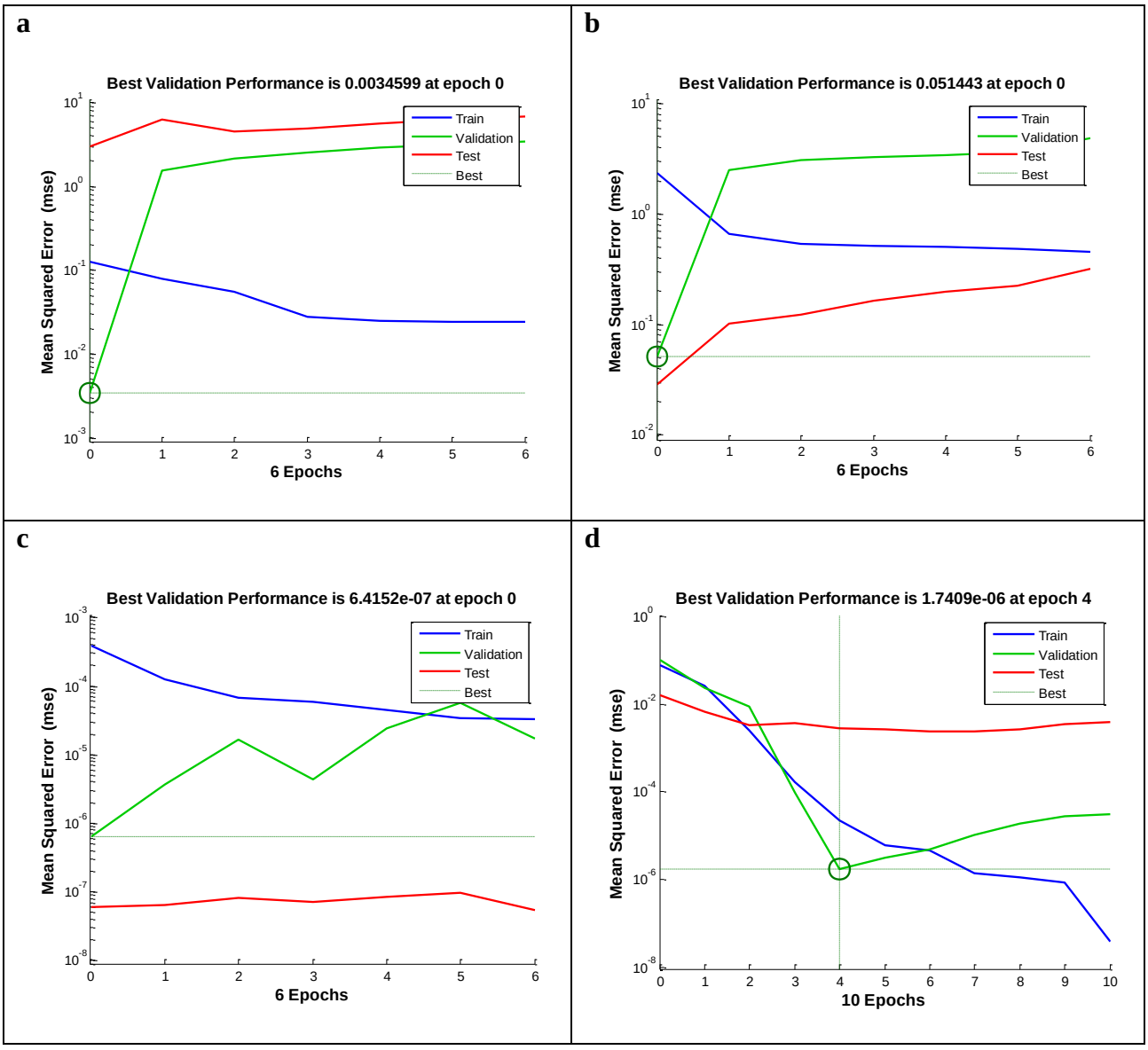

Fig. 4. ANN performance at 110 °C temperature by mean square error (MSE). (a) Autoclave temperature, (b) cold point temperature, (c) lethal rate, (d) TBA

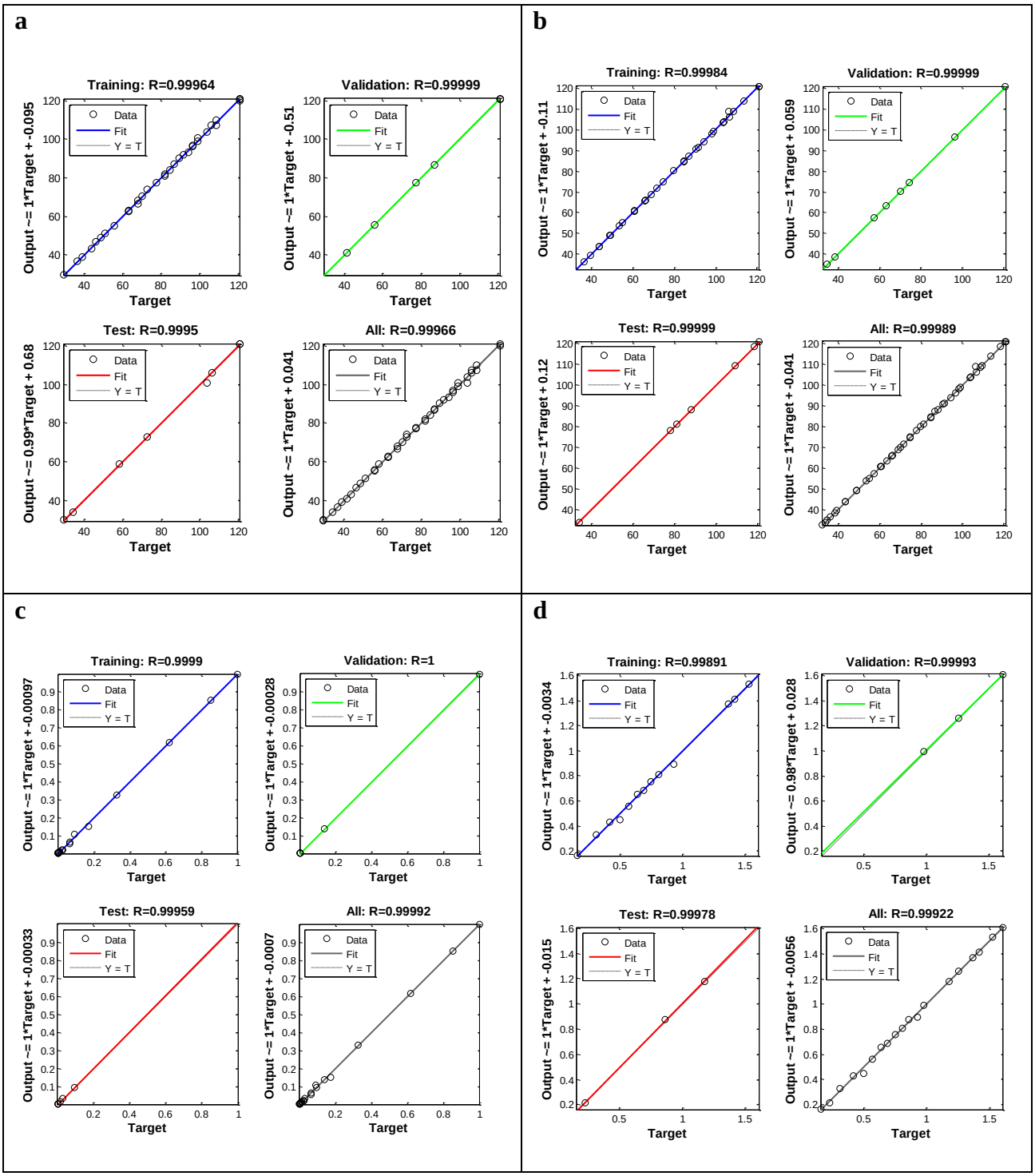

Fig. 5. ANN performance at 121 °C temperature via correlation coefficients (R). (a) Autoclave temperature, (b) cold point temperature, (d) lethal rate for training, validation, testing. The target data are experimental and the output data are the predicted

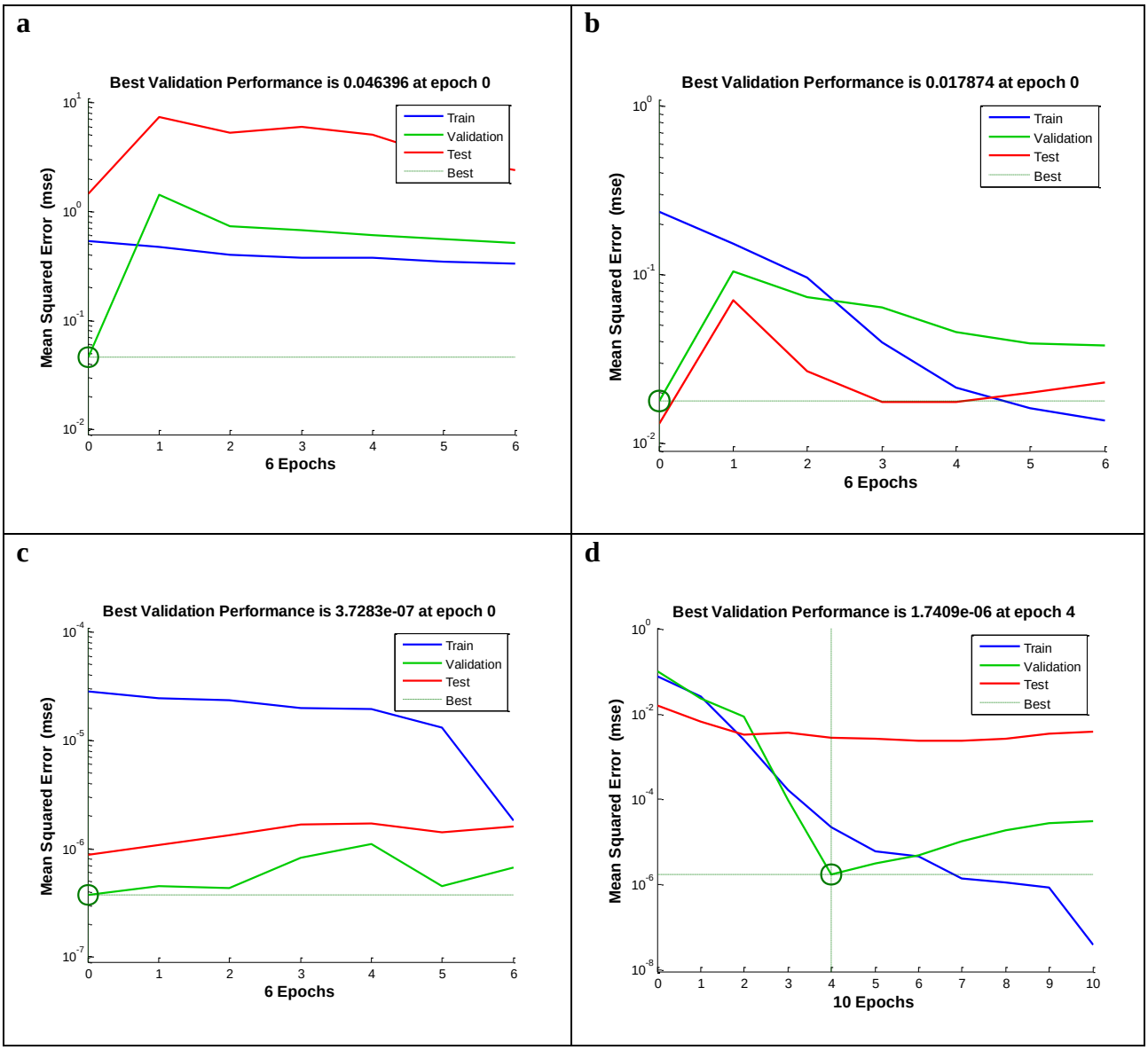

Fig. 6. ANN performance at 121°C temperature by mean square error (MSE). (a) Autoclave temperature, (b) cold point temperature, (c) lethal rate, and (d) TBA

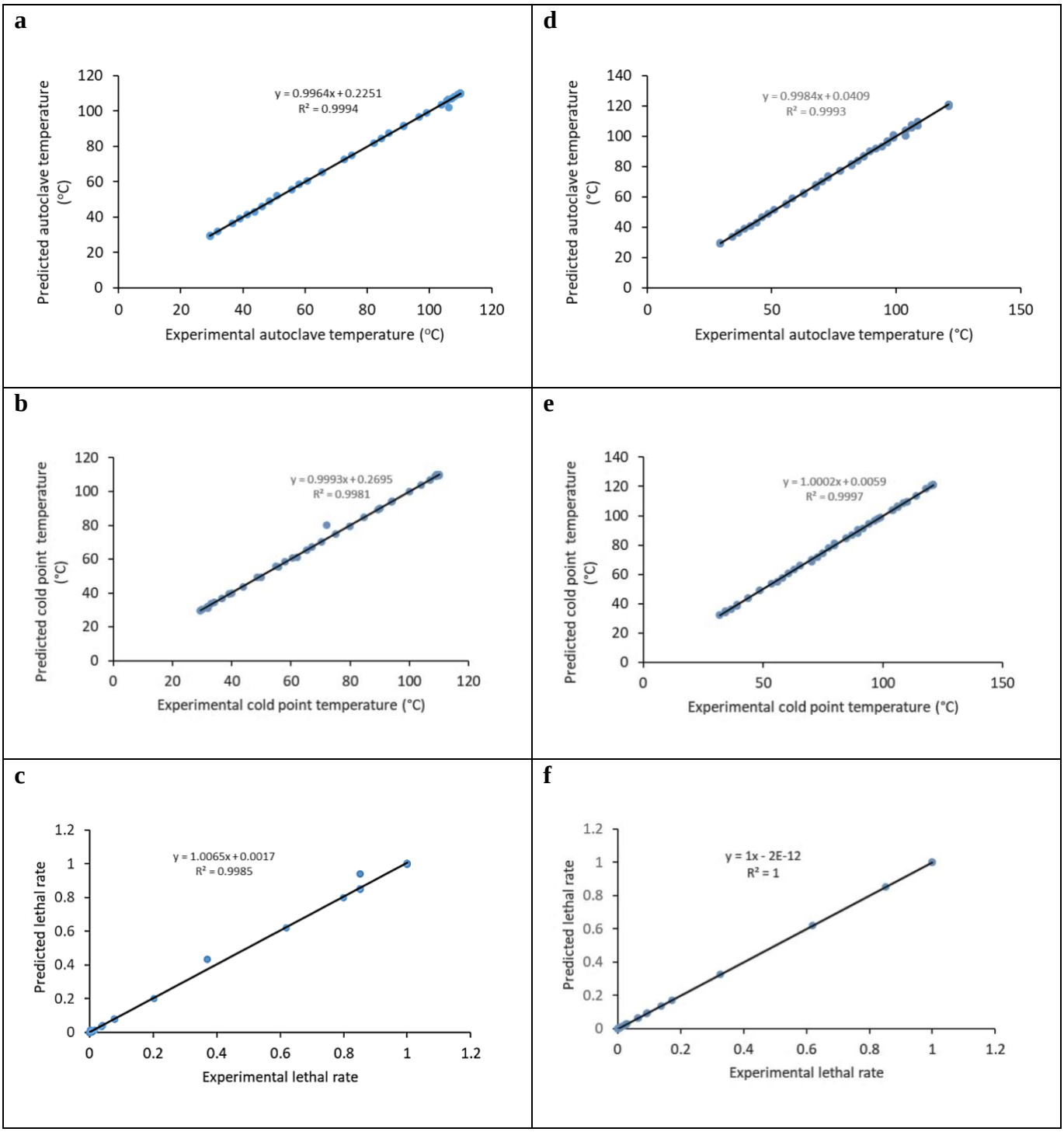

Fig. 7. Correlation coefficient between experimental and predicted of autoclave temperature, cold point temperature, and lethal rate at temperature of 110°C (a, b, c) and 121°C (d, e, f), respectively.

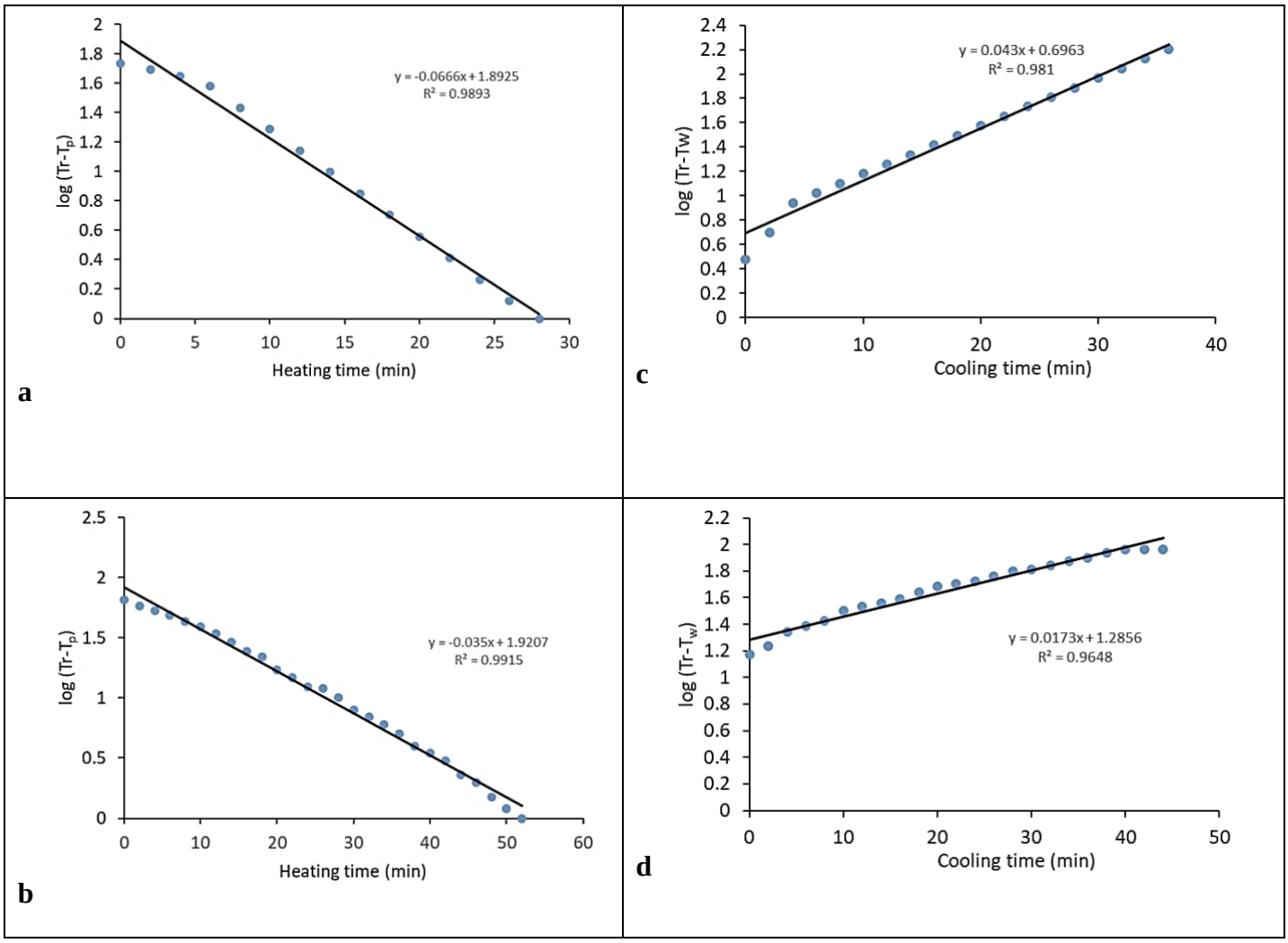

Fig. 8. Heating curve at (a) 110 °C, and (b) 121°C, cooling curve at (c) 110°C, and (d) 121°C

Table 1. Thermal evaluation of canned fish using the formula method of heating curve

Parameters of sterilization process	Temperature	
	110 °C	**121 °C**
T_{ih}	55.921	55.80
f_h	15.01	28.57
f_c	23.25	57.80
I_h	54.07	65.20
J_h	1.44	1.27
$J_h \times I_h$	78.07	83.31
f_i	1.42	0.89
U	33.67	15.36
f_h/U	0.44	1.85
J_c	1.45	1.10
log g	-1.512	0.26
g	0.03	1.840
$j_h i_h/g$	2538.04	45.25
$\log(j_h i_h/g)$	3.40	1.65
B_t	51.11	47.30
B	37.67	30.50

T_{ih} is the initial temperature of the canned fish at the start of the heating process (food temperature at the moment the steam is switched on, f_h and fc are the heat penetration factor of the canned fish (inverse slopes of heating and cooling curves (min)), I_h, difference between the temperature of heating medium and food temperature at the start of heating (^oC), J_h and J_c, heating and cooling lag factor of the canned fish (intercept coefficient of the heat penetration plot during heating and cooling), F_i is the period of heating in temperature T_r equivalent with heating of 1 minute in 121^oC (min), U is the time in minutes for sterilization at a temperature of the heating medium, log g is took from table ball formula, g is the difference between retort temperature and the temperature reached by the food at the point of concern (^oC), B_t is the total process time (min); and B (min) is the operator process time (time when retort reaches processing temperature until the steam is turned off).

TBA and determining the shelf life

Fig. (9a) shows the thiobarbituric acid values for canned and autoclaved Talang queen fish at a temperature of 110^{o}C and stored over a period of 18 months, where the thiobarbituric acid values for the period 0-18 months ranged between 0.11-1.39mg malondialdehyde/kg fish, respectively. The slight increase in TBA value can be attributed to the moderate thermal treatment, as noted by **Shanmugasundaram *et al.* (2019)**. High thermal treatments or long treatment periods lead to an increase in secondary oxidation products such as malondialdehyde. The results of the study differed from what was found by **El-Dengawy *et al.* (2012)**, who observed an increase in TBA values for raw shrimp after canning, rising from 0.40mg/ kg shrimp to 0.44 and 0.48mg/ kg in the canned

samples. They attributed this increase to the oxidation of unsaturated fatty acids present in the shrimp.

As shown in Fig. (9b), the thiobarbituric acid values for canned and autoclaved Talang queenfish fish at 121°C and stored for 18 months were between 0.16-1.61mg malondialdehyde/kg fish, respectively, for the period of 0-18 months. The increase in TBA value can be attributed to the high thermal treatment the fish were subjected to, as well as the extended storage period. **Rodríguez *et al.* (2009)** confirmed an increase in TBA value for the canned salmon with prolonged storage duration, rising from 1.5 to 1.9mg malondialdehyde/kg fish at the final storage period, attributing this to the thermal processes affecting the fats during primary and secondary oxidation due to exposure to high temperatures during the canning process. **El-Sherif and Abd El-Ghafour (2015)** found an increase in TBA values for canned tuna in tomato sauce and olive oil when stored for 6 months at laboratory temperature, rising from 2.54 and 2.75mg malondialdehyde/kg fish to 3.45 and 3.65mg malondialdehyde/kg fish at the final storage period, respectively. The TBA values in the current study are lower than the results of that study. As noted by **Rashid and Khidhir (2021)**, the TBA values of canned tuna increased with the extension of storage periods, reaching 0.437mg malondialdehyde/kg of fish at zero days to 0.782mg malondialdehyde/kg of fish at 60 days, attributing the increase to the oxidation of unsaturated fatty acids.

Cruz *et al.* (2022) found an increase in TBA values during the storage period of sardines packed in three types of packing solutions, including brine, oil, and tomato sauce. The TBA value increased from 3.54, 3.75, and 1.96mg malondialdehyde/kg to 4.40, 3.99, and 3.80mg malondialdehyde/kg at the end of storage, respectively. This was attributed to the stress caused by the effects of thermal processes in addition to the presence of the solution containing sodium chloride, which plays a role in the oxidation of unsaturated fatty acids. These results are higher than those obtained in the current study. **El-Shehawy and Farag (2019)** found that the TBA values in canned tuna fish reached 0.10mg malondialdehyde/kg fish, which is lower than our current study.

The two linear equations (20 and 21) were used to predict the TBA values for the canned and sterilized fish at temperatures of 110 and 121°C with an increased storage duration, where the statistical indicators were good: as follows:

SSE=0.02561, R-square: 0.9927, Adjusted R-square: 0.9922, RMSE: 0.03881 and SSE=0.04139, R-square: 0.9884, Adjusted R-square: 0.9878, and RMSE: 0.04934, respectively.

$$TBA_{110°C} = 0.07805t + 0.1542 \qquad (20)$$

$$TBA_{121°C} = 0.07877t + 0.1413 \qquad (21)$$

Where, t is the storage duration.

The slope in equations (20 and 21) represents the reaction rate constant (k), which equals 0.07805 and 0.07877mg malondialdehyde/kg, months at temperatures of 110 and 121°C, respectively. By rearranging equation (21), the shelf life of canned fish can be calculated, which was 15.83 months, while at a temperature of 121°C, the shelf life was 18.64 months.

$$t_{110^{\circ}C} = \frac{TBA - 0.1542}{0.07805} \qquad (22)$$

$$t_{121^{\circ}C} = \frac{TBA - 0.1413}{0.07877} \qquad (23)$$

pH

Fig. (10a) shows the pH values of canned and autoclaved Talang queenfish at a temperature of 110°C and stored for a period of 18 months, with pH values ranging from 6.10 to 6.32. **El-Sherif (2001)** attributed the increase in pH values in canned fish samples to the formation and accumulation of some basic amino acids and volatile basic nitrogen compounds such as NH_3 due to the breakdown of proteins during thermal treatments. The results of the study are consistent with those of **Czerner *et al.* (2015)** in their study on the effect of the canning process on the physical and chemical properties of *Engraulis anchoita*. It was found that the pH of fresh fish was 6.07, slightly increasing to 6.12 after canning.

Regarding the pH value (Fig. 10 b) which shows the pH values of canned and autoclaved Talang Queenfish fish at a temperature of 121°C and stored for 18 months, the effect of thermal treatments and the concentration of the saline solution played an effective role in raising the pH value. The results showed an increase in pH after canning that can be attributed to the increased concentration of pH-raising substances such as lactic acid. In other words, the loss of water from the tissues due to thermal treatments led to an increase in the concentration of lactic acid. The results of the study showed that the pH values are lower than those found by **Rashid and Khidhir (2021)** in their study on the effect of different storage temperatures on the quality of canned fish over storage periods of 0, 15, 30, and 60 days, where the pH values were 6.48, 6.26, 6.7, and 7.3, respectively. The increase was ascribed to the breakdown of fish proteins and the formation of compounds such as ammonia, amines, and hydrogen sulfide.

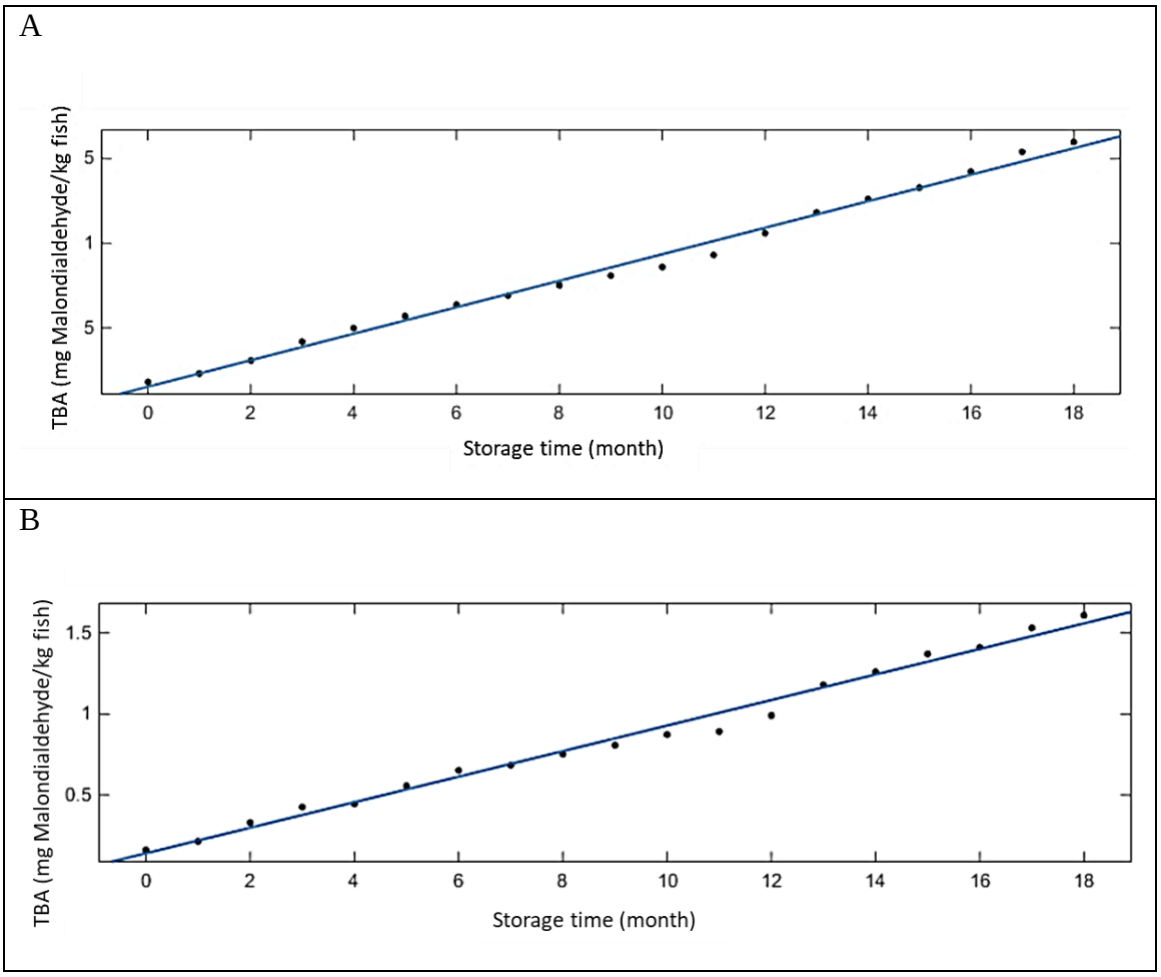

Fig. 9. Effect of storage period on the TBA a: 110ºC, and b: 121ºC of sterilized canned fish by autoclave

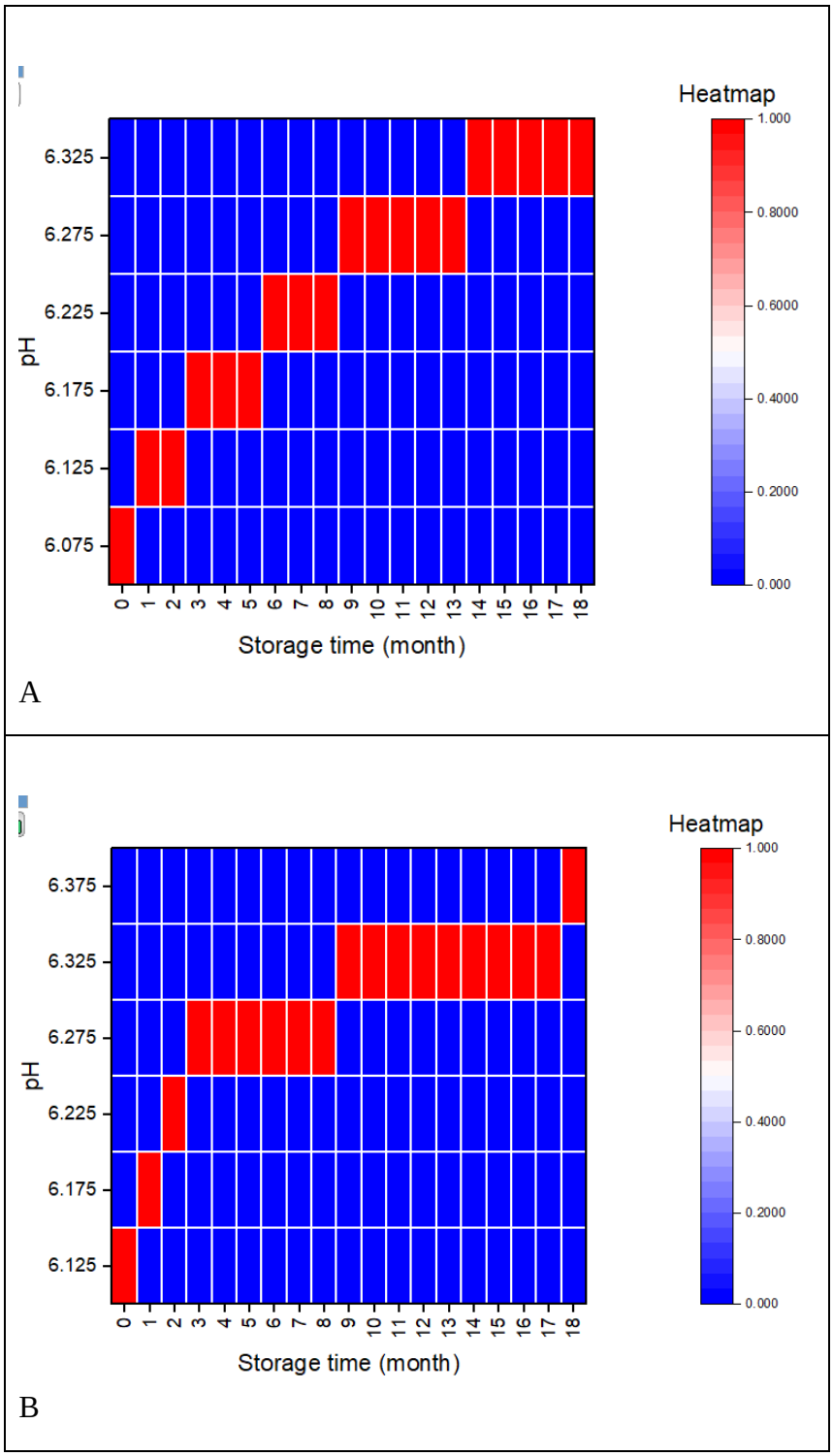

Fig. 10. Effect of storage time on the pH a: 110ºC, and b: 121ºC of sterilized canned fish by autoclave

CONCLUSION

The thermal process was designed to sterilize canned fish using an autoclave, modeling the temperatures with Artificial Neural Networks (ANN), and prediction of the shelf life. The prediction results using ANN for sterilizer temperatures, cold spot, and lethal rate showed a good fitting with the experimental results, with a very low error rate and a determination coefficient higher than 0.95. The lethal rate at temperatures of 121 and 110°C reached 1, which is the maximum value for the thermal kill rate. The value of the thermal penetration coefficient at the temperatures of 121°C was higher than at 110°C. Increasing the sterilization temperature enhanced the sterilization rate of the process, and all microorganisms in the sterilized containers were eliminated. The process time was 20min at 121°C according to the formula method used in the heat penetration study, resulting in a sterile and safe product. The thermal process time calculated using the formula method was shorter when using a temperature of 121°C compared to 110°C. The predicted shelf life of canned sterilized fish increased at a temperature of 121°C compared to 110°C. The study thus showed that verifying thermal processing methods using ANN can be applied to monitor sterilization processes in canning factories.

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