


Chemical components retention and modelling of antioxidant activity using neural networks in oven dried tomato slices with and without osmotic dehydration pre-treatment

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Abstract This study investigated the comparative retention of chemical and bioactive components in oven dried tomato slices with and without 10% saline osmotic dehydration (OD) pre-treatment. Antioxidant activity of tomato slices was modelled from phytochemical parameters using artificial neural networks (ANNs) trained with multilayer perceptron (MLP). Increase in water loss, solid gain, weight reduction and performance ratio obtained for tomato slices in 10% saline osmo-active solution indicated that moisture diffusion occurred faster than solid impregnation. Higher moisture diffusivity in slices with OD pre-treatment suggested faster water removal. A two-way ANOVA conducted revealed statistically significant effects of treatment methods, immersion time intervals and their synergistic interactions on moisture, ash, carbohydrate, energy, minerals (except sodium), antioxidant activity, flavonoid, lycopene, β -carotene contents. Statistical significance of both effects with non-significant and non-additive interactions were obtained for crude fat, crude protein, fatty acids, crude fibre and total phenols. Antioxidant activities modelled with ANNs had MLP architectures of 4-3-1 ($R^2=0.992$) and 4-3-2-1 ($R^2=0.995$) for oven dried tomato slices with and without OD pre-treatment respectively. High correlation coefficients $R^2=0.998$ (without OD pre-treatment) and $R^2=0.999$ (with OD pre-treatment) were obtained between

experimentally determined antioxidant activity using 2,2-diphenyl-1-picrylhydrazyl and modelled antioxidant activity using ANNs.

Keywords Artificial neural networks · Osmotic dehydration · Moisture diffusivity · Antioxidant activity

Introduction

Tomatoes (*Lycopersicon esculentum* Linn) are nutritional sources of vitamins (A, E and C), carotenoids (lycopene and β -carotene), polyphenols (phenolics, flavonoids and anthocyanins) and minerals (both macro and micro elements). These compounds are known to protect the body by scavenging free radicals, chelate ions and supply essential nutrients [1–6]. Tomatoes are highly perishable and decay rapidly if not processed [7]. They can be processed into cans, sachets and ketchups using different drying methods which could greatly affect the bioactive components and chemical compositions [8, 9].

Drying processes such as solar, convective, freeze, microwave, vacuum oven and infra-red drying have been reported to either improve or decrease nutritional composition, antioxidant activity, polyphenols and carotenoids contents [6, 10–13].

To optimise improvement in nutritional quality and minimise nutrient losses during drying processes, osmotic dehydration (OD) is usually employed as a pre-treatment method because it enhances drying rates, and preserves food materials fresher and better [14]. The preservation of nutritional components of tomatoes such as lycopene and β -carotene during OD pre-treatment contributes significantly to their functional properties [15]. OD involves soaking of food materials in osmo-active solution usually

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solutions of sugar and salt which allow partial dehydration of water with concomitant impregnation of solids from the solution [14–19].

Classical statistical methods have mostly been used to analyse and process data for evaluation of the contribution of phytochemicals to antioxidant activity whereas artificial neural networks (ANNs) provide viable alternatives for data processing, modelling and prediction. ANN have diverse uses and have been employed to predict inhibitory activity (LD_{50}) of coumarin derivatives [19], removal of nitrogen from waste water [20], water quality parameters [21], antioxidant activity of cruciferous sprouts [22], antioxidant activity of essential oils [23], classification and antioxidant activity of some teas [24], physicochemical and microbiological parameters of cherry tomato [25] and antioxidant activity and phenolic compounds of bananas subjected to different drying methods [26].

ANNs are mathematical algorithm developed to mimic the information processing as would be performed by the human brain. It has ability to simulate arbitrarily complex nonlinear processes that relate the inputs which are trained, tested and validated to predict the outputs. The model contains neurons that are richly interconnected by weighted connection lines and are adjusted when data are presented to the network during a “training” process [19, 21, 24, 27–29].

ANNs are defined by their architectures that show the organization of neurons layers; an input layer, hidden layer (s) and an output layer. These architectures are characterized by the transfer function indicating how the interconnections between neurons are made. There are several transfer functions whose selection depends on the problem being solved, ease of their implementation and optimization of algorithms. Multilayer perceptron (MLP) is the most used algorithm and it is a feed-forward network model [24, 28, 30].

Though different studies have reported the influence of OD on phytochemical contents and antioxidant activities but literature is still scanty on the effects of OD on chemical components such as proximate and mineral parameters. Equally, to the best of our knowledge, no study has reported the modelling of antioxidant activities from phytochemical contents for tomatoes subjected to OD pre-treatment using ANNs. Therefore, this study was undertaken to achieve these purposes.

Materials and methods

Reagents

Quercetin, Folin–Ciocalteu’s phenol, 2,2-diphenyl-1-picrylhydrazyl (DPPH), $NaCO_3$, $AlCl_3$ and CH_3OH used in the study are analar grade chemicals purchased from Sigma-Aldrich, Germany.

Samples

Tomato samples were bought at a farm in Oke-Osun, Osogbo, Osun State. They were Southern Nigeria tomato varieties. They were washed, blotted and cut into circular slices of 3 cm × 3 cm × 4 mm (length × breath × thickness).

Drying process

Osmotic pre-treatment of tomato slices

40 g of tomato slices were immersed into 10% saline solution (at 1:25 tomato: saline ratio) in a 2 L stainless steel container placed in a water bath. The bath was maintained at 35 °C for 60, 120, 180, 240 and 300 min. Tomato slices were removed after every 60 min, blotted and weighed.

Water loss (WL), solid gain (SG), weight reduction (WR) and performance ratio (PR) were calculated using Eqs. 1, 2, 3 and 4 respectively.

$$WL = \frac{(M_o - m_o)(M - m)}{m_o} \quad (1)$$

$$SG = \frac{m - m_o}{m_o} \quad (2)$$

$$WR = WL - SG \quad (3)$$

$$PR = \frac{WL}{SG} \quad (4)$$

where WL is the water loss, SG is solid gain and WR is weight reduction, PR is performance ratio, M_o is the initial mass of fresh tomato slices (g), M is the mass of tomato slices after time (t) of osmotic dehydration (g), m is the dry mass of tomato slices (g) after time (t) of osmotic dehydration and m_o is the initial dry mass of tomato slices (g).

Vacuum oven drying of tomato slices

30 g each of 4 mm tomato slices with and without OD pre-treatment were dried using vacuum oven (Uniscope SM 9053 Surgifriend Medicals England) at 105 °C. Samples were taken at 60, 120, 180, 240 and 300 min for the determination of antioxidant activity, phenolic, flavonoid, lycopene contents and chemical components.

Drying rate and moisture diffusivity of tomato slices

Drying rate of tomato slices with and without OD pre-treatment was calculated using Eq. 5

$$\frac{\Delta M}{\Delta t} = kM \quad (5)$$

where M is moisture content, k is drying rate and t is time (s).

Moisture diffusivity of tomato slices with and without OD pre-treatment was calculated using Eqs. 6–9.

$$MR = \frac{M_t}{M_i} \quad (6)$$

where M_i is the initial moisture content and M_t is the moisture contents at a particular time.

$$MR = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{2n+1} e^{-\frac{(2n+1)^2 \pi^2 D_{eff} t}{4L^2}} \quad (7)$$

$$MR = \frac{8}{\pi^2} e^{-\frac{\pi^2 D_{eff} t}{4L^2}} \quad (8)$$

where MR is moisture ratio, D_{eff} is moisture diffusivity ($m^2 s^{-1}$) and L is slice half thickness (m).

The D_{eff} was calculated from the slope of $\ln MR$ against t as shown in Eq. 9

$$D_{eff} = -\frac{\text{slope} 4L^2}{\pi^2} \quad (9)$$

Chemical composition of tomato slices

Proximate composition of tomato slices

Moisture, crude fibre, ash, crude fat and crude protein contents of tomato slices with and without OD pre-treatment were determined using methods of Association of Analytical Chemists [31]. Carbohydrate content was determined by difference. Energy content and fatty acid value were calculated using Eqs. 10 and 11 respectively

$$\text{Energy content} = 4(\text{protein}) + 4(\text{carbohydrate}) + 9(\text{crude fat}) \quad (10)$$

$$\text{Fatty acid value} = 0.8 \times \text{crude fat} \quad (11)$$

Mineral composition of tomato slices

The mineral contents such as potassium (K), magnesium (Mg), calcium (Ca), sodium (Na), manganese (Mn), iron (Fe), copper (Cu) and phosphorus (P) of tomato slices with and without OD pre-treatment were determined using methods of Association of Analytical Chemists [31] with atomic absorption spectrophotometer (AAS, S series 711047v1.22).

Determination of bioactive components

Extraction procedure

2 g of dried tomatoes powder was extracted twice with 150 ml of 70% aqueous methanol. The first extraction was done with 100 ml, shaken on orbital shaker for 90 min. and

filtered using Whatman No. 4 filter paper. The residue was further extracted with 50 ml following the previous procedure. Both filtrates were combined and concentrated using rotary evaporator at 40 °C.

Determination of antioxidant activity, total phenols and flavonoids contents

Antioxidant activity, total phenols and flavonoid contents of tomato slices with and without OD pre-treatment were determined using methods as reported by Azeez et al. [2].

Determination of carotenoids

The carotenoid content was analysed using modified extraction method of Takagi [32]. 5 g of oven dried tomato slices with and without OD pre-treatment was extracted with 75 ml of acetone, incubated in the dark at room temperature for 1 h and filtered using Whatman No. 4 filter paper. The residue was further extracted three times, filtrates were combined, concentrated using rotary evaporator at 70 °C and dried over anhydrous sodium sulphate. Dried extract was dissolved in methanol for gas chromatography coupled with flame ionization detector (GC-FID). 1 μ l of the methanolic extract was injected into GC (Hewlett–Packard Model 5890, USA) with FID which has AC-5 column (30 m \times 0.25 μ m \times 0.25 mm id), nitrogen as a carrier gas, a detector section temperature of 320 °C with a split ratio of 20:1 and mode inlet section temperature of 250 °C. The column was initially set at 60 °C, increased at 10 °C/min for 20 min, maintained for another 20 min. and at 15 °C for 4 min and maintained for another 4 min. Concentrations of lycopene and β -carotene were quantified from calibration curves of lycopene and β -carotene standards.

Artificial neural networks (ANNs) modelling of antioxidant activity

ANN was employed to model the antioxidant activity of oven dried tomato slices with and without OD pre-treatment based on data of phytochemical contents. MLP was used as the architecture model with back propagation algorithm and stratified sampling procedure was used for splitting. For modelling of antioxidant activity in tomato slices without OD pre-treatment, 60% of the data was used for training and 40% for testing while for slices with OD pre-treatment, 57.1% of data was used for training and 42.9% for testing. This action of neural networks was determined by the weights applied in the hidden and output nodes. There were more weights in MLP with OD pre-treatment than without OD.

Four covariates (phenolics, flavonoids, lycopene and β -carotene) were used in the input layer with normalized rescaling method. Hyperbolic tangent was the activation function used for neurons in the hidden layer (s). Identity function was used for neurons in the output layer with standardized rescaling method of scale dependent.

MLP architecture for tomato slices without OD pre-treatment had one hidden layer containing three neurons having a neural network architecture of 4-3-1. Tomato slices with OD pre-treatment had two hidden layers with three and two neurons in each layer giving an architecture of 4-3-2-1.

Statistical analysis

Data of bioactive and chemical components were expressed as mean \pm standard deviation of three replicates. A Two-way ANOVA was conducted to determine the effects of two treatment methods, five immersion time intervals, and interactions between treatment methods and time intervals on bioactive, chemical and mineral contents of tomato slices at 95% confidence level using SPSS software (IBM SPSS Statistics 20, Chicago, USA). R statistical software package (Rstudio.Ink) was used for running the ANN. Evaluation of goodness of fit between DPPH and ANN antioxidant activities was determined by correlation coefficient (R^2) and the root mean square error (RMSE)

$$RMSE = \sqrt{\left[\frac{1}{n} \sum_{i=1}^n (X_{exp,i} - X_{pred,i})^2 \right]} \quad (12)$$

$X_{exp,i}$ is the i th experimentally determined antioxidant activity, $X_{pred,i}$ is the i th ANN predicted antioxidant activity and n is the number of observations.

Results and discussion

Drying process

Osmotic pre-treatment

Osmotic dehydration pre-treatment of tomato slices in 10% saline solution was studied in terms of WL, SG, WR and PR. The results are presented in Figs. 1 and 2 respectively. Increase in WL, SG, WR and PR was observed with increase in time of immersion of tomato slices in osmotic solution. This could have resulted from higher osmotic driving potential of the solution that occurred with increase in time of immersion. Similar results have been reported by Ispir and Togrul [33], Singh et al. [34], Abraao et al. [35], Ahmed et al. [36], and Correa et al. [37].

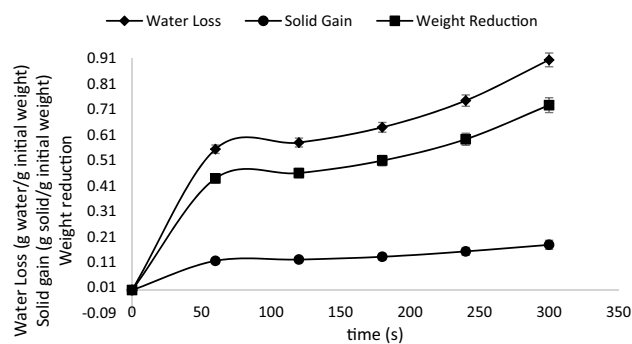


Fig. 1 Effects of immersion time on water loss, solid gain and weight reduction in osmotic dehydrated tomato slices

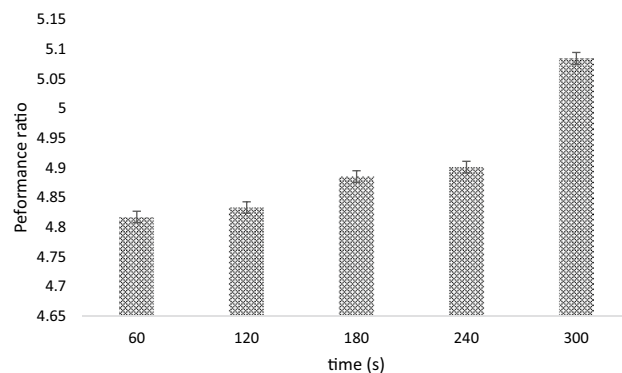


Fig. 2 Performance ratio of water loss and solid in osmotic pre-treated tomato slices

Increase in PR is indicative of dehydration process effectiveness and faster rate of water loss relative to solid uptake [38]. In this study, PR was found to increase with increase in time of immersion (Fig. 2) which suggest effective dehydration process. This result is similar to results of Abraao et al. [36] and Saini [38].

Drying rate and moisture diffusivity of tomato slices

The result of drying rate and moisture diffusivity (D_{eff}) of oven dried tomato slices with and without OD pre-treatment are presented in Fig. 3 and Table 1 respectively. Drying rate and Moisture diffusivity of oven dried tomato slices with OD pre-treatment were higher than without OD pre-treatment. This indicates moisture diffusion in slices with OD pre-treatment occurred faster than in tomato slices without OD pre-treatment [6]. This could be due to the effect of osmotic dehydration pre-treatment which opened pores within the tissue of tomato slices thereby allowing for faster moisture loss [36]. The values of D_{eff} are within the range of 10^{-12} to 10^{-8} m^2/s that has been reported tomatoes [39, 40].

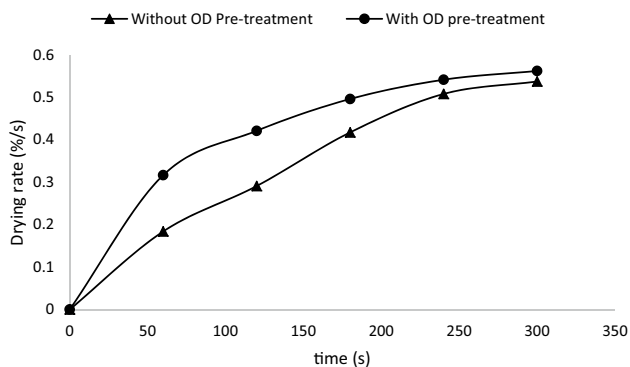


Fig. 3 Drying rate of oven dried tomato slices with and without OD pre-treatment

Table 1 Moisture diffusivities of oven dried tomato slices with and without OD pre-treatment

Treatment	D_{eff} (m^2/s) $\times 10^{-9}$
Osmotic pre-treatment	2.52
Untreated	2.41

Proximate composition of tomato slices

The results of proximate composition of oven dried tomato slices with and without OD pre-treatment are presented in Table 2. Tomato slices with and without OD pre-treatment had decrease in moisture, crude protein, ash, crude fat, fatty acid contents and increase in crude fibre, carbohydrate, energy contents with increasing drying time compared to raw. Slices with OD pre-treatment had lower moisture, ash, crude fat, crude protein, fatty acid contents and higher crude fibre, carbohydrate and energy contents compared to slices without OD pre-treatment. Two-way ANOVA conducted on the results of proximate contents revealed statistically significant effects of treatment methods and immersion time intervals on decrease in moisture $F(4, 20)=82.961, p=0.00$ (for both), ash $F(4, 20)=3.476, p=0.00$ (for both), crude fat $F(4, 20)=0.905, p=0.44, 0.00$ (treatment, time), crude protein $F(4, 20)=2.693, p=0.01, 0.00$ (treatment, time) and fatty acids $F(4, 20)=0.962, p=0.04, 0.00$ (treatment, time). There were statistically additive significant interactions between effects of treatment methods and immersion time intervals on decrease in moisture ($p=0.00$), ash ($p=0.026$) while the interactions between both effects were statistically non-additive and non-significant on decrease in crude fat ($p=0.48$), crude protein ($p=0.61$) and fatty acids ($p=0.45$). There were statistically significant effects of treatment methods and immersion time intervals on increase in crude

Table 2 Chemical composition of oven dried tomato slices with and without OD pre-treatment

Time (min)	Moisture (g/100 g)		Ash (g/100 g)		Crude fibre (g/100 g)		Crude fat (g/100 g)		Crude protein (g/100 g)		Carbohydrate (g/100 g)		Energy (kcal/100 g)		Fatty acid (g/100 g)	
	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD
Raw	91.19±0.72		1.11±0.03		1.01±0.13		3.08±0.11		2.47±0.17		1.14±0.02		42.16±0.16		2.46±0.09	
60	80.16±0.08	72.20±0.07	1.08±0.01	0.85±0.05	2.02±0.07	2.11±0.01	3.05±0.56	3.01±0.03	2.27±0.12	2.13±0.03	11.42±0.04	19.70±0.04	82.21±1.41	114.41±0.76	2.44±0.02	2.41±0.25
120	73.74±0.58	65.94±0.18	1.02±0.02	0.81±0.03	2.75±0.18	2.92±0.11	3.02±0.35	2.91±0.19	2.18±0.06	2.09±0.07	17.29±0.03	25.33±0.22	105.06±3.22	135.87±3.67	2.42±0.04	2.33±0.06
180	66.16±0.66	61.44±0.44	0.93±0.02	0.78±0.03	3.06±0.14	3.30±0.07	2.43±0.63	2.06±0.28	1.97±0.08	1.71±0.03	25.45±0.09	30.71±0.17	131.55±4.65	148.22±4.92	1.94±0.10	1.65±0.15
240	60.73±0.13	58.72±0.16	0.92±0.01	0.76±0.01	3.27±0.17	3.45±0.01	2.14±0.08	1.82±0.26	1.52±0.02	1.53±0.03	31.42±0.74	33.72±0.09	151.02±5.40	157.38±1.28	1.71±0.14	1.46±0.26
300	58.97±0.17	57.48±0.41	0.90±0.01	0.68±0.02	4.02±0.32	4.64±0.28	2.15±0.19	1.73±0.33	1.28±0.15	1.21±0.03	32.68±0.39	34.26±0.21	155.19±7.13	157.45±3.10	1.72±0.12	1.38±0.32

Un untreated, OD osmotic dehydration pre-treatment. Data are mean ± standard deviation of three replicates

fibre $F(4, 20)=2.114, p=0.00$ (for both), carbohydrate $F(4, 20)=172.039, p=0.00$ (for both) and energy $F(4, 20)=16.972, p=0.00$ (for both). Statistically significant interaction between the effects on increase in carbohydrate ($p=0.00$) and energy ($p=0.00$) was additive while a statistically non-significant and non-additive interaction between the effects was obtained for crude fibre ($p=0.117$).

The results in this study have comparable contents of moisture, ash and crude fibre for raw tomato slices to those obtained for tomatoes by Pinela et al. [4] and Guil-Guerrero and Reboloso-Fuentes [41] but with higher contents of crude fat, crude protein, energy and lower content of carbohydrate.

Decrease in moisture contents with increasing drying time and further decrease in slices with OD pre-treatment indicate that shelf-stability of oven dried tomato slices got improved with drying time and better with OD pre-treatment because it accelerated moisture removal faster which support rottenness [2, 6]. Also, decreases in protein, ash, crude fat and fatty acid content with increasing drying time suggest there could have been denaturation and solubilisation of nitrogenous compounds, loss of fat and essential minerals during drying. These results are similar to trends reported by Gonçalves et al. [42], Nwaoguikpe et al. [43], Avola et al. [44]. Further reduction in protein and ash contents of slices with OD pre-treatment could have resulted from the leaching of organic compounds and minerals during OD [6, 36]. Lower fat and fatty acid contents obtained for slices with OD pre-treatment suggest that the slices may be less prone to lipid deterioration [5].

Significantly higher contents of crude fibre, carbohydrate and energy contents in slices with OD pre-treatment show that the oven dried tomato slices would better enhance digestibility, reduce cholesterol, prevent bowel cancer and supply higher energy [5, 42, 43].

Mineral contents of tomato slices

Mineral compositions of oven dried tomato slices with and without OD pre-treatment are presented in Table 3. Na, K, Ca, Fe, P and Cu decreased while Mg, and Mn contents increased with drying time in oven dried tomato slices without OD pre-treatment compared to raw. Slices with OD pre-treatment had increased Na, Mg contents and reduced contents of K, Ca, Mn, Fe, P and Cu compared to raw. Comparing mineral contents of tomato slices with and without OD pre-treatment, slices with OD pre-treatment had higher Na, Mg contents and lower K, Ca, Mn, Fe, P and Cu contents. Two-way ANOVA conducted on the results of mineral contents showed statistically significant effects of treatment methods and immersion time intervals on sodium $F(4, 20)=47.881, p=0.00$ (treatment), potassium $F(4, 20)=30.625, p=0.00$ (for both), calcium $F(4, 20)=3.058,$

Table 3 Mineral contents of oven dried tomato slices with and without OD pre-treatment (mg/kg, tomato dried basis)

Time (min)	Sodium (Na)		Potassium (K)		Calcium (Ca)		Magnesium (Mg)		Manganese (Mn)		Iron (Fe)		Phosphorus (P)		Copper (Cu)	
	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un	OD
Raw (0)	11.85 ± 0.03		25.01 ± 0.01		3.16 ± 0.13		3.06 ± 0.03		0.17 ± 0.01		0.028 ± 0.01		1.56 ± 0.02		0.013 ± 0.00	
60	11.62 ± 0.04	12.50 ± 0.03	24.55 ± 0.12	23.22 ± 0.02	3.10 ± 0.02	3.04 ± 0.02	3.22 ± 0.02	3.33 ± 0.03	0.35 ± 0.01	0.17 ± 0.01	0.026 ± 0.00	0.017 ± 0.00	1.23 ± 0.02	1.20 ± 0.01	0.011 ± 0.00	0.011 ± 0.00
120	11.52 ± 0.12	13.03 ± 0.02	24.25 ± 0.02	23.03 ± 0.03	2.84 ± 0.12	2.77 ± 0.01	3.19 ± 0.01	3.29 ± 0.01	0.32 ± 0.01	0.17 ± 0.01	0.024 ± 0.00	0.017 ± 0.00	1.16 ± 0.01	1.09 ± 0.02	0.009 ± 0.00	0.01 ± 0.00
180	10.47 ± 0.04	13.58 ± 0.03	23.77 ± 0.07	22.41 ± 0.03	2.51 ± 0.06	2.34 ± 0.01	3.17 ± 0.01	3.26 ± 0.02	0.24 ± 0.01	0.15 ± 0.00	0.017 ± 0.00	0.016 ± 0.00	1.13 ± 0.00	0.82 ± 0.01	0.007 ± 0.00	0.01 ± 0.00
240	10.09 ± 0.83	14.01 ± 0.04	21.84 ± 0.22	21.17 ± 0.03	2.22 ± 0.11	2.11 ± 0.02	3.09 ± 0.02	3.17 ± 0.02	0.20 ± 0.01	0.15 ± 0.00	0.013 ± 0.00	0.016 ± 0.00	1.12 ± 0.01	0.77 ± 0.01	0.006 ± 0.00	0.009 ± 0.00
300	10.02 ± 0.01	14.42 ± 0.12	20.52 ± 0.04	20.05 ± 0.10	1.78 ± 0.04	1.52 ± 0.02	3.07 ± 0.01	3.10 ± 0.01	0.18 ± 0.01	0.12 ± 0.01	0.011 ± 0.00	0.016 ± 0.00	1.07 ± 0.02	0.69 ± 0.01	0.005 ± 0.00	0.007 ± 0.00

Un untreated, OD osmotic dehydration pre-treatment. Data are mean ± standard deviation of three replicates

$p=0.00$ (for both), magnesium $F(4, 20)=4.850$, $p=0.00$ (for both), manganese $F(4, 20)=60.563$, $p=0.00$ (for both) and phosphorus $F(4, 20)=226.853$, $p=0.00$ (for both). There was a statistically non-significant effect of immersion time on sodium content ($p=0.401$). There were statistically additive significant interactions between effects of treatment methods and immersion time intervals on sodium ($p=0.00$), potassium ($p=0.00$), calcium ($p=0.041$), magnesium ($p=0.07$), manganese ($p=0.00$) and phosphorus ($p=0.00$).

The results in this study have higher Na but lower contents of other mineral contents in raw tomatoes compared to results of Guil-Guerrero and Reboloso-Fuentes [41] on mineral contents of tomatoes.

The reduction obtained for macro elements (Na, K, Ca and Mg) in this study during drying is similar to results reported by Avola et al. [44] and Lewu et al. [45] on effects of cooking on mineral contents of cocoyam and chickpeas. This might not be unconnected with the decrease in ash content with increasing drying time. Increase in Mg and Mn contents could have resulted from breakaway of the bonds between these minerals and tissues of tomato slices during drying [41]. Equally, further increase in Na content of tomato slices with OD pre-treatment might have resulted from impregnation of salt during OD pre-treatment while reduction in other minerals could have resulted from loss during moisture diffusion in OD pre-treatment [6].

The ratios of Na/K and Ca/P are presented in Table 4. Na/K and Ca/P ratios varied irregularly with drying time in tomato slices without OD pre-treatment but increased with drying time in slices with OD pre-treatment.

The ratio of Na/K in the body is of great importance in the control of high blood pressure. Na/K ratio of <1 is recommended. All Na/K ratios for tomato slices in this study were lower than 1 (though tomato slices with OD pre-treatment had higher values) indicating that dried tomato slices using these processes could be used in lowering blood pressure [46]. Ca/P ratio higher than 1 indicates that the food is good for maintaining bone health and preventing reduction

Table 4 Ratios of mineral contents in oven dried tomato slices with and without OD pre-treatment

Time (min)	Na/K		Ca/P	
	Un	OD	Un	OD
Raw	0.42		2.03	
60	0.48	0.54	2.52	2.53
120	0.48	0.57	2.45	2.54
180	0.44	0.61	2.22	2.85
240	0.46	0.66	1.98	2.70
300	0.49	0.72	1.66	2.20

Un untreated, OD osmotic dehydration pre-treatment

Table 5 Antioxidant activity, phenolic, flavonoid, lycopene and β -carotene contents oven dried tomato slices with and without OD pre-treatment

Time (min)	Flavonoid content (mg quercetin/g of extract)		Phenolic content (mg quercetin/g of extract)		Lycopene content ($\mu\text{g}/100\text{ g}$)		β -carotene content ($\mu\text{g}/100\text{ g}$)		Antioxidant activity (%)	
	OD	Un	OD	Un	OD	Un	OD	Un	OD	Un
Raw	75.88 \pm 2.02		261.68 \pm 5.81		25.05 \pm 0.27		78.81 \pm 1.01		92.08 \pm 1.72	
60	69.66 \pm 0.07	63.33 \pm 0.33	247.26 \pm 7.22	236.25 \pm 2.38	23.51 \pm 0.53	24.48 \pm 0.32	74.19 \pm 0.19	63.67 \pm 0.75	89.57 \pm 1.34	76.33 \pm 0.72
120	61.37 \pm 1.18	54.66 \pm 0.67	230.75 \pm 2.86	222.18 \pm 2.74	21.72 \pm 0.22	20.14 \pm 0.46	70.92 \pm 0.28	62.21 \pm 0.12	87.27 \pm 0.12	76.04 \pm 0.06
180	56.15 \pm 0.73	44.81 \pm 0.71	224.21 \pm 3.67	218.38 \pm 4.66	19.54 \pm 0.21	18.75 \pm 0.14	64.74 \pm 0.12	60.72 \pm 0.39	86.35 \pm 0.24	72.44 \pm 0.25
240	51.91 \pm 1.26	38.63 \pm 0.11	207.11 \pm 2.93	206.08 \pm 1.24	17.91 \pm 0.23	15.43 \pm 0.04	62.57 \pm 0.07	57.24 \pm 0.21	78.82 \pm 0.15	69.19 \pm 0.55
300	48.02 \pm 0.28	37.35 \pm 0.27	202.19 \pm 1.27	190.27 \pm 3.05	14.23 \pm 0.01	13.02 \pm 0.13	58.63 \pm 0.03	50.55 \pm 0.11	76.35 \pm 0.38	64.47 \pm 0.07

Un untreated, OD osmotic dehydration pre-treatment. Data are mean \pm standard deviation of three replicates

in bone mineral density [47, 48]. As obtained in this study, Ca/P ratios were higher 1 suggesting that dried tomato slices consumption would not be harmful to bone health.

Antioxidant activity, phytochemicals and carotenoids contents of tomato slices

The results of antioxidant activity, total phenols, flavonoid, lycopene and β -carotene contents of tomato slices with and without OD pre-treatment are presented in Table 5. The bioactive components decreased with increase in drying time and lower compared to raw. Their contents in tomato slices with OD pre-treatment were significantly higher than in slices without OD pre-treatment.

Two-way ANOVA conducted on the results of bioactive contents revealed statistically significant effects of treatment methods and immersion time intervals on flavonoid $F(4, 20)=28.409, p=0.00$ (for both), total phenols $F(4, 20)=2.241, p=0.00$ (for both), lycopene $F(4, 20)=29.178, p=0.00$ (for both), β -carotene $F(4, 20)=126.226, p=0.00$ (for both) and antioxidant activity $F(4, 20)=14.618, p=0.00$ (for both). There were statistically additive significant interactions between effects of treatment methods and immersion time intervals on flavonoid ($p=0.00$), lycopene ($p=0.00$), β -carotene ($p=0.00$), antioxidant activity ($p=0.00$) while the interactions between both effects were statistically non-additive and non-significant on total phenols ($p=0.101$).

Decrease in contents of bioactive components during drying obtained in this study is similar to results of previous studies done on the contents of polyphenols, antioxidant activity, lycopene and β -carotene contents of sour cherry fruits, bananas, tomatoes, [6, 13, 15, 49–51].

Significantly higher contents of bioactive components obtained for tomato slices with OD pre-treatment indicate that the pre-treatment decreased their degradation during drying which would improve the nutritional quality of final tomato products. This is similar to reports of previous study that foods with OD pre-treatment preserved bioactive compounds better than conventional methods only [15, 37, 52]. This study has shown that drying with OD pre-treatment is an effective method of tomato preservation [25].

Modelled antioxidant activity using ANNs

Multilayer perceptron (MLP) with back propagation algorithm was employed to model the antioxidant activities of oven dried tomato slices with and without OD pre-treatment based on phenolic, flavonoid, lycopene and β -carotene contents.

The number of neurons in hidden layer was determined as a function of sum of squares error, mean square error, correlation coefficient and relative error of the trained ANN. The model summaries containing all these are listed in Tables 6 and 7.

MLP architecture for tomato slices without OD pre-treatment had one hidden layer containing three neurons having a neural network architecture of 4-3-1. Tomato slices with OD pre-treatment had two hidden layers with three and two neurons in each layer giving an architecture of 4-3-2-1. MLP developed for both processes are shown in Fig. 4a, b. Parameter estimates of developed MLP are presented in Tables 6 and 7. Different MLP structures of tomato slices with or without OD pre-treatment was based on neural networks weights applied in the hidden and output nodes. There were more weights in MLP with OD pre-treatment than without OD.

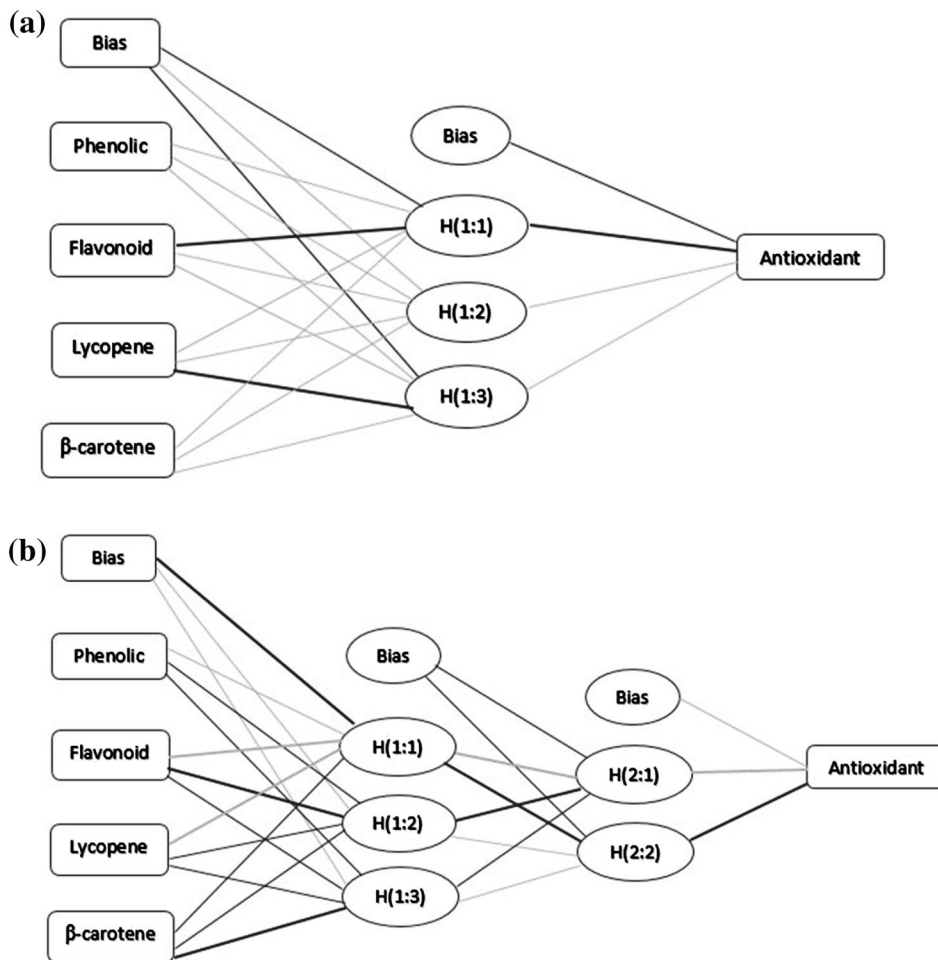
Table 6 Model summary and parameter estimates of developed MLP for oven dried tomato slices without OD pre-treatment

	Model summary		Predictor	Predicted			
	Training	Testing		Hidden layer			Output layer
				H (1:1)	H (1:2)	H (1:3)	
Sum of squares error	0.28	0.26					
Relative error	0.16	0.09	Input	Bias	-0.215	0.483	-0.257
Mean square error		0.293		Phenolic	0.162	0.394	0.365
Correlation coefficient		0.992		Flavonoid	-0.635	0.048	0.544
				Lycopene	0.365	0.295	-0.914
				β -carotene	0.040	0.214	0.132
			Hidden layer	Bias			-0.098
				H (1:1)			-0.563
				H (1:2)			0.299
				H (1:3)			0.985

Table 7 Model summary and parameter estimates of developed MLP for oven dried tomato slices with OD pre-treatment

	Model summary		Predictor	Predicted						
	Training	Testing		Hidden layer 1			Hidden layer 2		Output layer	
				H (1:1)	H (1:2)	H (1:3)	H (2:1)	H (2:2)	Antioxidant	
Sum of squares error	0.23	0.03								
Relative error	0.65	0.05	Input	Bias	-0.522	0.150	0.083			
Mean square error		0.322		Phenolic	0.492	-0.542	-0.120			
Correlation coefficient		0.995		Flavonoid	0.211	-0.073	-0.044			
				Lycopene	0.498	-0.210	-0.356			
				β-carotene	-0.029	-0.254	-0.368			
			Hidden layer 1	Bias				-0.214	-0.176	
				H (1:1)				0.638	-0.310	
				H (1:2)				-0.605	0.254	
				H (1:3)				-0.366	0.194	
			Hidden layer 2	Bias						0.280
				H (2:1)						0.955
				H (2:2)						-0.402

Fig. 4 a MLP architecture for modelling antioxidant activity in oven dried tomato slices without OD pre-treatment. **b** MLP architecture for modelling antioxidant activity in oven dried tomato slices with OD pre-treatment



Analysis of variance of each factor in the model and the model as a whole was tested for its ability to account for variation in the dependent variable (antioxidant activity).

The model for all the factors indicates a statistically significant effect of each factor on antioxidant activity. The adjusted R^2 indicates that the factors had 99 and 97%

variations on the antioxidant activity in tomato slices with and without OD pre-treatment respectively. The sum of squares for corrected model and corrected total of tomato slices with OD pre-treatment were 259.336 and 260.659 respectively with an error of 1.322 while the sum of squares for corrected model and corrected total of slices without OD pre-treatment were 155.584 and 116.463 with an error of 0.879.

Test for the homogeneity of the covariate parameter estimates against the dependent variable at 95% confidence level, showed that interaction terms ($t_{\text{calculated (without OD pre-treatment)}} = 1.33$ and $n_{\text{calculated (with OD pre-treatment)}} = 0.76$) were significant indicating that the covariate parameter estimates were not homogenous. Since the interaction terms were significant, the difference between their effects for different values of antioxidant activity was significant.

The model-estimated marginal means and standard error of antioxidant at the factor combinations of phenolic, flavonoid, lycopene and β -carotene are useful for exploring the possible interaction effect between these four factors. It was found for tomato slices with OD pre-treatment that phenolic had highest interaction with antioxidant of about 307.11 ($R^2=0.949$), followed by flavonoid with interaction value of 73.28 ($R^2=0.972$), β -carotene with the interaction value of 59.38 ($R^2=0.916$) and lycopene had about 28.02 ($R^2=0.945$). The grand interaction mean of the four factors and antioxidant was 84.28 with standard error of 1.353 ($R^2=0.974$).

For tomato slices without OD pre-treatment, phenolic also had highest interaction with antioxidant of about 258.43 ($R^2=0.944$), followed by β -carotene with interaction value of 65.30 ($R^2=0.924$), flavonoid with the interaction value of 64.43 ($R^2=0.981$) and lycopene had about 11.21 ($R^2=0.824$). The grand interaction mean of the four factors and antioxidant was 79.84 with standard error of 0.243 ($R^2=0.944$).

The predictive accuracy between ANN modelled and experimentally determined antioxidant activities was evaluated using correlation coefficient (R^2) and RMSE. The model is considered accurately fit if R^2 is close to 1 and the value of RMSE is low. The plots of ANN modelled antioxidant activity against DPPH determined antioxidant activities for tomato slices with and without OD pre-treatment are shown in Fig. 5a, b. The straight line patterns in these plots indicate that linear relationship exists between modelled and experimentally determined antioxidant activities. Low RMSE and high R^2 values of both tomato slices with and without OD pre-treatment indicate ANN accurately modelled the antioxidant activities.

The normalized importance indicating the contribution of each phytochemical parameter to modelled antioxidant activity is presented in Fig. 6. Lycopene had the highest contribution in terms of importance to antioxidant activities

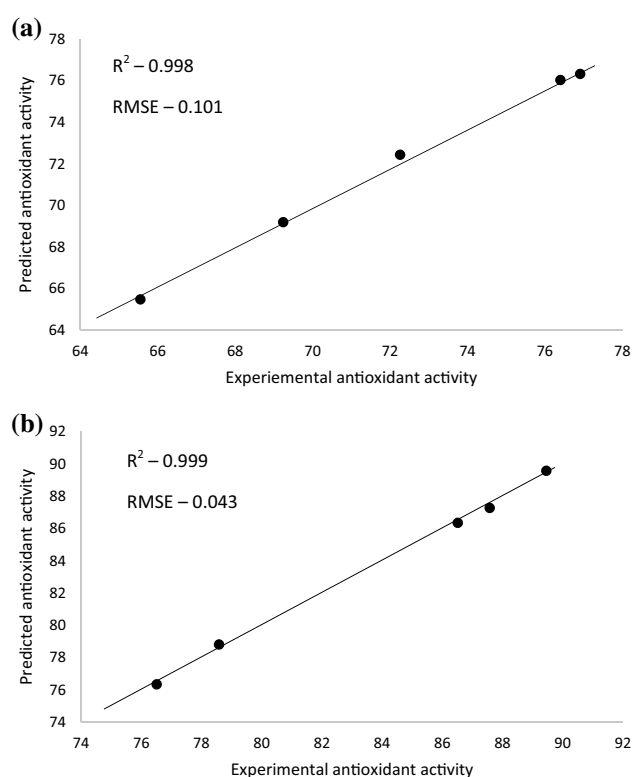


Fig. 5 **a** Regression plot of modelled and experimentally determined antioxidant activity of oven dried tomato slices without OD pre-treatment. **b** Regression plot of predicted and experimentally determined antioxidant activity of oven dried tomato slices with OD pre-treatment

for both methods of preservations while β -carotene contributed the least. It has been reported previously in studies that quality of tomatoes is determined by its lycopene content [3, 53].

Conclusion

This study has reported the comparative retention of proximate, minerals, antioxidant activity, polyphenols and carotenoids in oven dried tomato slices with and without osmotic dehydration (OD) pre-treatment. Artificial neural networks were used to model antioxidant activity based on data from phytochemical parameters. Tomato slices with OD pre-treatment had faster water removal rate. OD pre-treatment was able to decrease the degradation of bioactive components during drying. ANNs with multiplayer perceptron modelled antioxidant activities correlated strongly with experimentally determined antioxidant activities using DPPH method. This study has shown that drying with osmotic pre-treatment is an effective method of tomato slices preservation.

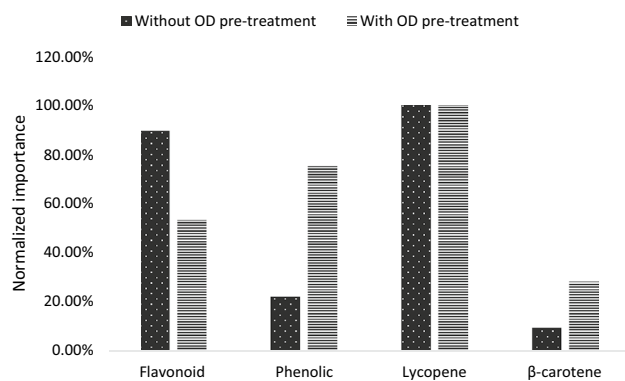


Fig. 6 Percentage contribution of each phytochemical to modelled antioxidant activities in oven dried tomato slices with and without OD pre-treatment

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