

DOI: 10.7251/QOL2401029K

UDC: 632.64-295.4.028:621.38

Original scientific paper

MODELING OF MICROWAVE-ASSISTED EXTRACTION OF LYCOPENE FROM TOMATO PEELS

STEFAN KUVENDZIEV, MARTIN STOJCHEVSKI, MARTINA ANDREEVSKA, VIOLETA LUKANOVSKA,
MIRKO MARINKOVSKI, KIRIL LISICHKOV

Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University in Skopje, N. Macedonia, mirko@tmf.ukim.edu.mk

ABSTRACT: Dry tomato peels were investigated as a natural source of lycopene in this study. Microwave-assisted extraction (MAE) was used for the isolation of bioactive compound of interest. The MAE was performed at a microwave power of 120, 230, and 385 W for a duration of 2, 5, 8, and 10 min. The concentration of lycopene in the separated extract with n-hexane was quantified by UV/Vis spectrophotometer. The absorbance at 501 nm was selected for the determination of lycopene content and the calculation of lycopene yield (mg/100 g). An adequate feedforward artificial neural network (ANN) model with architecture 2-10-1, trained by the Levenberg-Marquardt (LM) back-propagation algorithm was developed for modeling the MAE process and for the prediction of the lycopene yield. The model predicted lycopene yield with a high coefficient of determination $R^2=0.9957$ and low mean squared error $MSE=0.475$. The response surface methodology (RSM) was successfully applied and combined with the ANN model to optimize the MAE process with $R^2=0.9477$ and a low mean absolute error $MAE=1.84507$. The analysis of variance showed that extraction time and time-squared have statistically significant effects on the lycopene yield. The created 3D response surface showed that the optimum lycopene yield was 27.25 mg/100g of tomato peels at the microwave power of 324 W and extraction time of 8.6 min.

Keywords: lycopene, tomato peels, microwave-assisted extraction, artificial neural network modeling.

INTRODUCTION

Industries based on the processing of agricultural products produce a tremendous amount of bio-waste (industrial by-products) every year. Biomass is considered one of the most valuable energy and raw material sources (Sadh et al, 2018). Over the last few years, using waste materials from numerous industries has garnered considerable attention as a sustainable approach to resource management and environmental protection. Industrial by-products are cheap, renewable, abundant raw materials, rich in bioactive compounds, and can be used as alternative sources for obtaining new products, including biochemical products, biomaterials, biogas, etc (Babu et al, 2022; Messinese et al, 2023). Tomato processing industries generate significant amounts of waste by-products, including tomato peels, which are usually dumped and contribute to environmental pollution. However, tomato peels are also a natural source of biologically active compounds that contribute to their nutritional and potential healthy beneficial effects. Tomato peels contain lycopene, beta-carotene, vitamins C and E, phenolic compounds, flavonoids, fibers, minerals, etc (Laranjeira et al, 2022). Lycopene is highly concentrated in tomato peels, making them a rich source of this carotenoid pigment (Zuorro, 2020).

Lycopene or ψ,ψ -carotene is a red carotenoid pigment and is the most abundant carotenoid in ripe tomatoes (approximately 80-90% of the total pigments) (Cadoni et al, 1999), as well as in watermelon, apricot, pink grapefruit, guava, etc (Xi, 2006). This compound has an anti-inflammatory effect (Hazewindus et al, 2012) and it is a well-known powerful natural antioxidant that scavenges free radicals in the body (Imran et al, 2020), and in nature mainly exists in the all-*trans* form, but it can be degraded through the processes of *cis-trans* isomerization and oxidation, due to its high sensitivity to light, heat, and oxygen (Shi et al, 2002). Lycopene has many positive benefits on human health, including cancer prevention, skin protection, im-

proving eye health and cardiovascular system, and osteoporosis prevention (Khan et al, 2021; Walallawita et al, 2020). Hence it is widely applied in the food, cosmetics, pharmaceuticals, and textile industries. In recent years, there has been a growing interest in using waste by-products from the food industry to extract bioactive compounds, and tomato peels represent a valuable source for the extraction of lycopene, so its recovery from tomato peels represents a sustainable solution for both waste management and the production of a valuable natural pigment (Trombino et al, 2021). Various extraction techniques have been applied for lycopene separation from natural matrixes, such as maceration, ultrasound-assisted extraction, microwave-assisted extraction, enzyme-assisted extraction, and supercritical fluid extraction (Catalkaya & Kahveci, 2019; Kehili et al, 2019; Lianfu & Zelong, 2008; Rahimi & Mikani, 2019). Conventional extraction techniques are less efficient, time-consuming processes that are performed in several steps, using a larger amount of solvent. On the other hand, non-conventional extraction techniques, such as microwave-assisted extraction (MAE), are more efficient and selective, environmentally friendly, and provide the preservation of heat-sensitive compounds due to reduced extraction time (Bitwell et al, 2023).

Microwave-assisted extraction (MAE) is a modern extraction technique that is intensively employed for the isolation of compounds from plant material. MAE is a process of using electromagnetic radiation with a frequency of 0.3-300 GHz (Chan et al, 2011). Heat and mass transfer in MAE is different compared to conventional methods. In conventional solid-liquid extraction, heat transfer takes place from the liquid to the solid phase, while mass transfer occurs from the solid to the liquid phase. Contrarily in the MAE the heat and mass are transferred from the solid to the liquid. During the MAE, microwave energy penetrates the sample and generates heat internally. This results in the disruption of cell structures and provides extraction time reduction and better penetration of compounds from the matrix to the solvent (Sadeghi et al, 2017). Understanding these processes and proper control of microwave power, extraction time, and sample-solvent interactions is necessary to ensure effective heat and mass transfer during the MAE. In microwave-assisted extraction, several parameters affect on the efficiency and the yield of extracted compounds of interest such as extraction time, solvent type, microwave power, sample-solvent ratio, sample size, etc (Alara et al, 2018; Pengdee et al, 2020). Modeling the process is an essential step for achieving an efficient and selective extraction process, and obtaining high-quality extracts. Artificial neural networks (ANNs) are often used to model and predict complex processes such as microwave-assisted extraction (Simić et al, 2013; Sinha et al, 2013).

In this study, in order to model the microwave-assisted extraction process and predict the yield of lycopene extracted from tomato peels as a function of the extraction time and microwave power, an appropriate artificial neural network was created.

MATERIALS AND METHODS

MATERIALS

Fresh ripe tomatoes (*Solanum lycopersicum*) used in this study as a raw material for obtaining tomato peels were purchased from a local market in Skopje, N. Macedonia. The tomato peels were separated by using a commercial electric peeling machine. Obtained tomato peels were immersed in the 1% potassium metabisulfite solution for 3 min to inhibit the growth of microorganisms and protect the material from molds. Pre-treated peels were dried at 30°C to moisture less than 10%. The average moisture content of the homogenized material was 8.24%. The particle size of the working raw material was in the range of 0.315-3.15 mm. The raw material was vacuumed in plastic bags and stored in a refrigerator at a temperature of 4°C. The prepared tomato peels were employed for the extraction of lycopene by using microwave-assisted extraction. n-Hexane (for analysis, Merck) was used for the isolation of lycopene from tomato peels.

MICROWAVE-ASSISTED EXTRACTION PROCESS

The microwave-assisted extraction process was done in a created system for microwave-assisted extraction by using a modified commercial microwave oven (Superior Technology, maximum power of 700 W). Tomato peels 2 g and 40 ml of n-hexane (1:20 sample to solvent ratio w/v) were placed into a 250 ml round bottom flask and fixed into the oven. The bottom flask was connected to a condenser. The microwave-assisted extraction system is illustrated in Figure 1. After finishing the extraction, the sample was immediately filtered through a filter paper with a pore size of 25 μm . Inert residues were separated on the filter paper. The n-hexane was vaporized from the extract in a rotary vacuum evaporator (Büchi R-200). The dried residue represented the total extract and the yield of the total extract was determined. Subsequently, the total extract was dissolved in the n-hexane, and the concentration of the lycopene was measured.

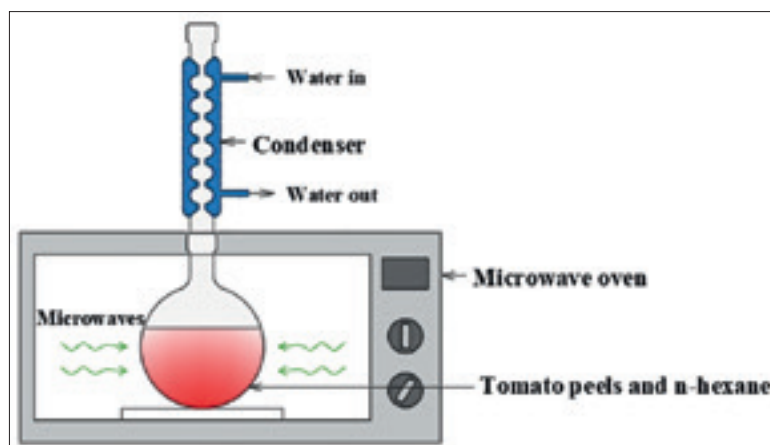


Figure 1. Schematic of the microwave-assisted extraction system for recovering lycopene from tomato peels

In this study, the influence of extraction time t and microwave power P on the yield of lycopene was investigated. MAE was performed at a microwave power of 120, 230, and 385 W for a duration of 2, 5, 8, and 10 min.

DETERMINATION OF LYCOPENE YIELD

The concentration of lycopene in the prepared solution was quantified by using a UV/Vis spectrophotometer (Spectroquant® Prove 600). The measurement was performed at 25°C in the wavelength range of 300-600 nm with a peak detection of 0.05 and $\Delta\lambda=1$ nm. A rectangular quartz glass cuvette with a 10 mm path length was used for analysis. n-Hexane as a blank solution was employed to automatically adjust the baseline.

The yield of lycopene y_L (mg/100 g of tomato peels) was calculated by:

$$y_L = \frac{0.00312 A V_E D}{m_S} \quad (1)$$

where: A is the absorbance at 501 nm, V_E is the volume of extract (ml), D is the dilution coefficient, and m_S is the mass of the sample (kg).

ANN MODELING OF MAE

Artificial neural networks (ANNs) have often been used to model complex relations between independent input data and dependent output data. An artificial neural network is a statistical model of learning inspired by biological neural networks. ANN is a technique for generating a prediction of output variables such as the concentration of target compounds or extraction yield. The effectiveness of ANN modeling de-

depends on data quality, ANN architecture, hyperparameter tuning, activation functions, training, validation, and testing of the created model.

ANN model was created and developed to model and optimize the microwave-assisted extraction process of lycopene from tomato peels, i.e. for predicting the lycopene yield as a function of extraction time and microwave power. The ANN model was designed in MATLAB-Neural Network Toolbox. The extraction time and microwave power were used as input values so the ANN contained two neurons in the input layer. The yield of lycopene was employed as a target value hence the output layer contained one neuron. The optimal number of neurons in the hidden layer as a crucial parameter was verified by determining the minimum value of mean squared error (MSE). The MSE is mathematically calculated by:

$$MSE = \frac{1}{n} \sum_{i=1}^n (X_{pi} - X_{ai})^2 \quad (2)$$

where n is the number of all observations, X_{pi} is a predicted value generated from the model, and X_{ai} is an actual value obtained from the experiments. Response surface methodology (RSM) was applied and combined with the ANN model to optimize the MAE process, mathematical model fitting, graphical response surface representation, and analysis of the importance of investigated operating parameters. RSM model was developed in Statgraphics Centurion XV.

The evaluation of adequacy and efficiency of the model was determined by the MSE, the coefficient of determination (R^2), and the mean absolute error (MAE).

$$R^2 = 1 - \frac{\sum_{i=1}^n (X_{pi} - X_{ai})^2}{\sum_{i=1}^n (X_{ai} - X_m)^2} \quad (3)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |X_{pi} - X_{ai}| \quad (4)$$

where X_m is the average of the actual values.

RESULTS AND DISCUSSION

Microwave-assisted extraction of lycopene from tomato peels with n-hexane was performed at working conditions as described previously, in order to determine and model the influence of extraction time t and microwave power P on the lycopene yield. The UV/Vis absorption spectrum of each obtained extract contained three characteristic peaks of lycopene at 444, 470, and 501 nm (Figure 2). To avoid interference of other carotenoids, the absorbance at 501 nm was selected for the determination of lycopene content in the extract.

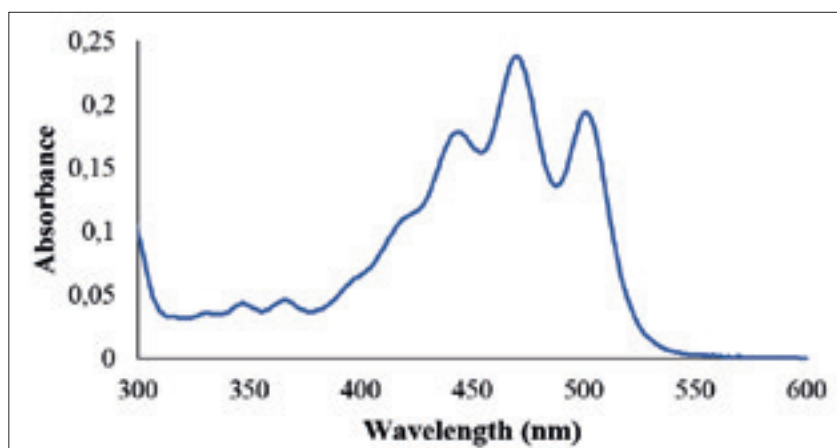


Figure 2. The UV/Vis absorption spectrum of the lycopene extracted with n-hexane from tomato peels by using MAE ($t=2$ min, $P=120$ W)

An adequate artificial neural network model was developed for modeling the microwave-assisted extraction process and for the prediction of the lycopene yield from tomato peels obtained by using n-hexane as a solvent. The development of the appropriate ANN model based on the experimental values involved several steps, from data collection and splitting to model training and evaluation. Choosing from the several types, a feedforward neural network (FNN) was built and trained by using the Levenberg-Marquardt (LM) algorithm to adjust the weights during the backpropagation process. The values of extraction time and microwave power were used as an input matrix in the ANN model. The experimentally obtained yields of lycopene were used as a target matrix in the model. The model was trained by using 60% of the data set and the training involved optimizing weights and calculating the error between the predicted and the actual target output. The performance and precision of the ANN were monitored through the validation and testing steps. The data set was split into training, validation, and test sets, containing 60% for training, 20% for validation, and 20% for testing. The optimal number of neurons in the hidden layer with nonlinear hyperbolic tangent activation function was determined at a minimum MSE. Different numbers of neurons in the range of 2-12 in the hidden layer were analyzed (Figure 3).

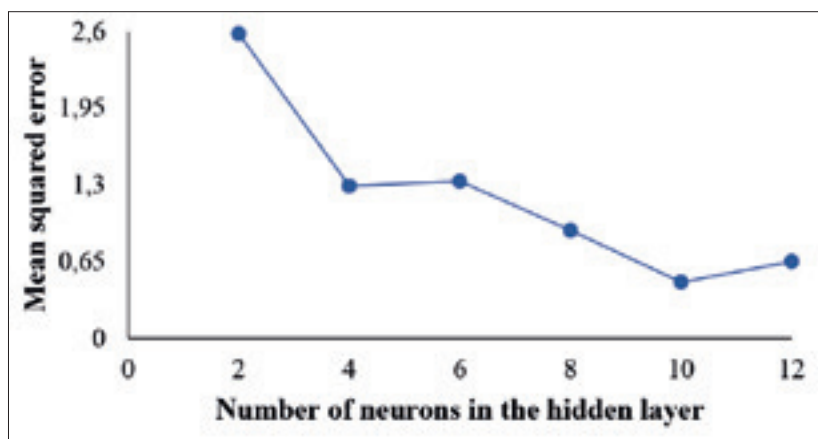


Figure 3. The relation between the number of neurons in the hidden layer and the mean squared error

The created ANN model with architecture 2-10-1 generated an output matrix of predicted lycopene yield y_{LANN} versus experimentally obtained actual lycopene yield y_L with a high coefficient of determination $R^2=0.9957$ and low mean squared error $MSE=0.475$. The visual relations between the predicted outputs of the model and the actual target for the training, validation, testing, and all are given in Figure 4. The scatter plots also show that the ANN model adequacy and efficiency predicted the actual data with high correlation coefficients of 1, 0.99821, and 0.997494 for training, validation, and testing, respectively.

The error histogram shown in Figure 5 provided additional verification of the network performance, where most data fall on the zero error line. It generally suggests that each pair of data is a good fit and the ANN model mathematically describes the MAE process well. The utilized ANN model adequately predicted the lycopene yield from tomato peels obtained in the operating range of 0-10 min and 120-385 W (Figure 6).

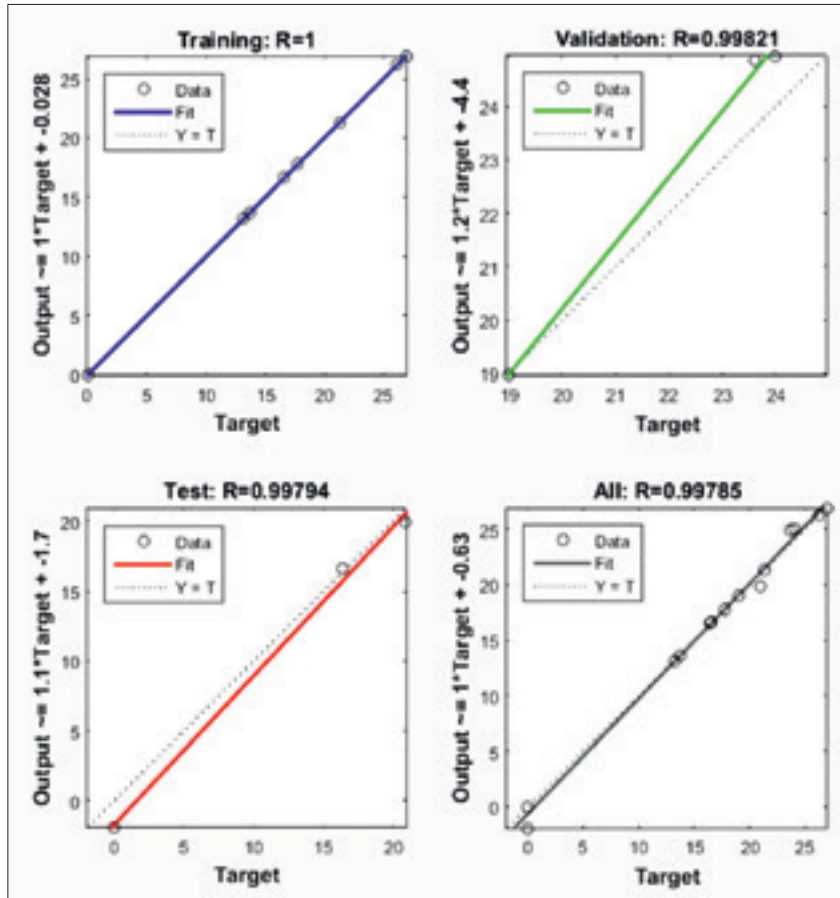


Figure 4. ANN regression plots for training, validation, testing, and all data sets

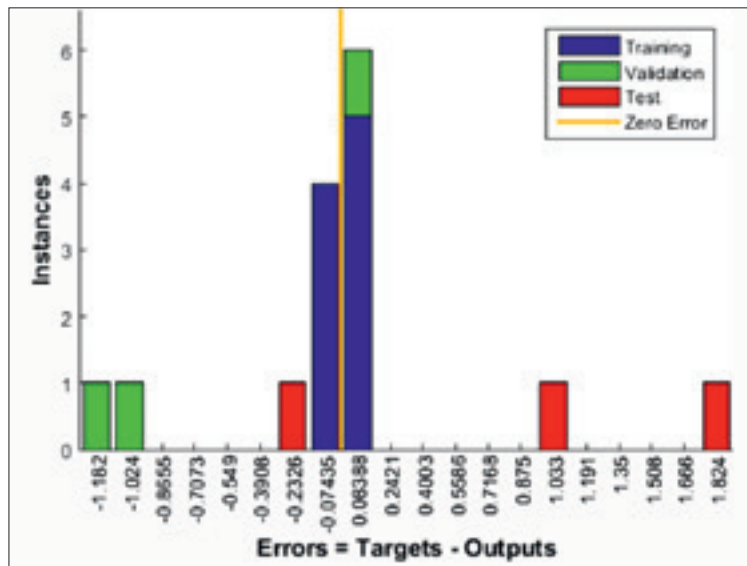


Figure 5. Plot error histogram for the ANN model

The RSM was used to optimize the ANN model and determine the effects of extraction time and microwave power on the lycopene yield, as well as to define the optimum MAE region. The RSM efficiently fitted the ANN predicted yield of lycopene y_{LANN} with a high coefficient of determination $R^2=0.9477$ and a low mean absolute error $MAE=1.84507$. The standardized Pareto chart (significance level, $\alpha=0.05$) for the considered process is shown in Figure 7. The chart shows that the extraction time (A), the interaction between extraction time and microwave power (AB), and the microwave power (B) have a positive effect

on the lycopene yield, while the extraction time-squared (AA) and the microwave power-squared (BB) influence negatively. However, the extraction time and extraction time-squared have statistically significant effects on the lycopene yield.

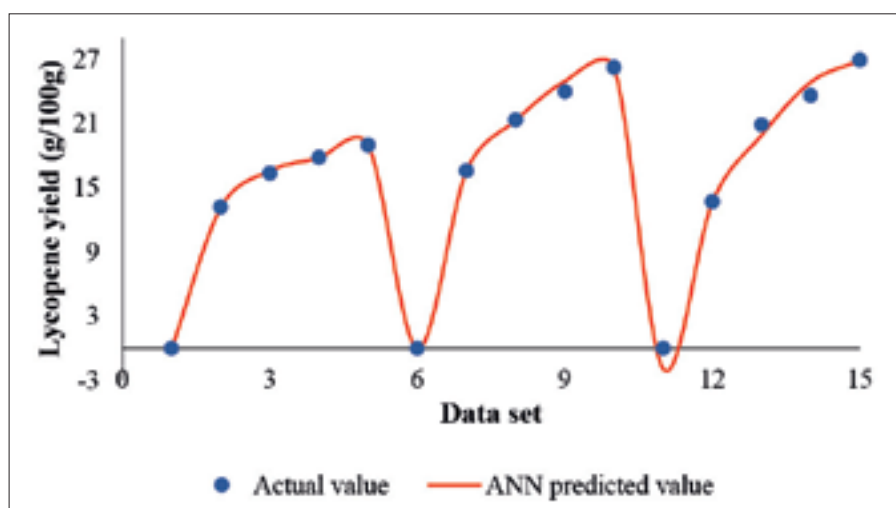


Figure 6. A comparative plot of ANN predicted lycopene yield and experimentally obtained lycopene yield

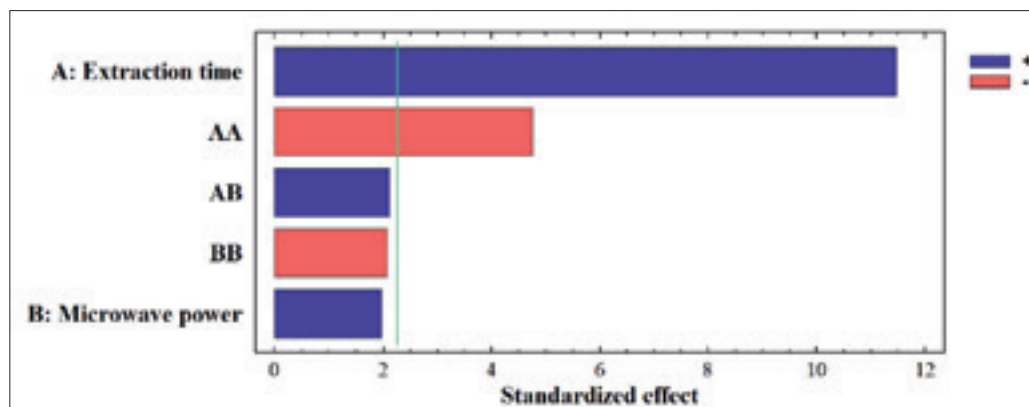


Figure 7. Pareto chart of relative importance and standardized influence of operating parameters on the lycopene yield

The regression equation was utilized to empirically describe the relation between the studied operating parameters and ANN-predicted lycopene yield. The relation was mathematically defined using the following equation:

$$y_{LANN} = -6.8851 + 4.6669 t + 0.0866 P - 0.3404 t^2 + 0.0037 t P - 0.0002 P^2 \quad (5)$$

A 3D response surface was created to visually present the effects and interactions of independent factors on the response (y_{LANN}). The response surface is given in Figure 8, where the axes represent the levels of inputs (time and power), and the vertical axis represents the ANN-predicted lycopene yield.

The response surface shows that the increase of extraction time in the region of 0-8.5 min results in the lycopene yield increase, but in this interval the increase of microwave power does not significantly influence in lycopene yield increase. After approximately 8.5 min to 10 min, the effect of time on the lycopene yield is insignificant, however, the increase in microwave power leads to the lycopene yield increasing. The response surface and analysis of variance showed that the optimum lycopene yield is 27.25 mg/100g at the microwave power of 324 W and extraction time of 8.6 min.

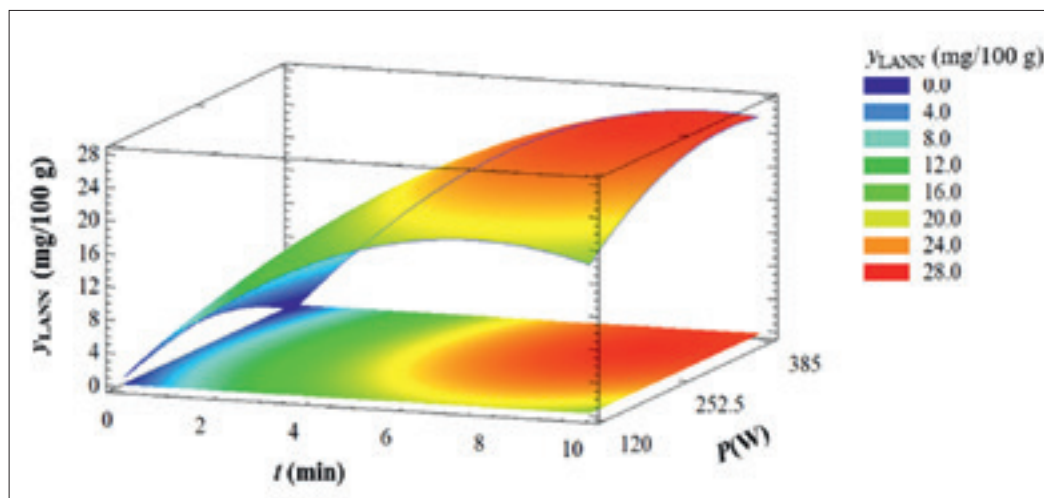


Figure 8. Response surface plot for the microwave-assisted extraction of lycopene from tomato peels

CONCLUSION

The recovery of lycopene from tomato peels with n-hexane by using microwave-assisted extraction was investigated in this study. The tomato peels were selected as a low-cost and renewable natural source of lycopene which usually has been generated by various industries as a waste by-product. The non-conventional microwave-assisted extraction technique provided a high lycopene yield in a short period of time. The artificial neural network model with architecture 2-10-1 was successfully developed and used to model the complex influence of extraction time and microwave power on the lycopene yield. The ANN model produced an output matrix of predicted lycopene yield versus experimentally obtained yield with $R^2=0.9957$ and $MSE=0.475$. The created model adequately predicted the lycopene yield from dry tomato peels in the operating range of 0-10 min and 120-385 W. The RSM with a high coefficient of determination $R^2=0.9477$ and a low mean absolute error $MAE=1.84507$, was applied and combined with the ANN model to optimize the MAE process. The statistical analysis showed that extraction time, microwave power, and their interaction influence positively, while time-squared and power-squared had a negative effect on the lycopene yield. The optimal yield of lycopene was achieved (27.25 mg/100g) at the microwave power of 324 W for a duration of 8.6 min.

ACKNOWLEDGEMENTS

The present research is part of a project funded by the Ministry of Education and Science of North Macedonia (project financing decision number: 08-15590/5) and co-funded by Bionika Pharmaceuticals.

REFERENCES

- Alara, O. R., Abdurahman, N. H., & Olalere, O. A. (2018). Optimization of microwave-assisted extraction of flavonoids and antioxidants from *Vernonia amygdalina* leaf using response surface methodology. *Food and Bioproducts Processing*, 107, 36-48. <https://doi.org/10.1016/j.fbp.2017.10.007>.
- Babu, S., Singh Rathore, S., Singh, R., Kumar, S., Singh, V. K., Yadav, S. K., Yadav, V., Raj, R., Yadav, D., Shekhawat, K., & Ali Wani, O. (2022). Exploring agricultural waste biomass for energy, food and feed production and pollution mitigation: A review. *Bioresource Technology*, 360. <https://doi.org/10.1016/j.biortech.2022.127566>.
- Bitwell, C., Indra, S. sen, Luke, C., & Kakoma, M. K. (2023). A review of modern and conventional extraction techniques and their applications for extracting phytochemicals from plants. *Scientific African*, 19. <https://doi.org/10.1016/j.sciaf.2023.e01585>.
- Cadoni, E., Rita De Giorgi, M., Medda, E., & Poma, G. (1999). Supercritical CO₂ extraction of lycopene and β -carotene from ripe tomatoes. *Dyes and Pigments*, 44(1), 27-32. [https://doi.org/10.1016/S0143-7208\(99\)00065-0](https://doi.org/10.1016/S0143-7208(99)00065-0).
- Catalkaya, G., & Kahveci, D. (2019). Optimization of enzyme assisted extraction of lycopene from industrial tomato waste. *Separation and*

- Purification Technology, 219, 55-63. <https://doi.org/10.1016/j.seppur.2019.03.006>.
- Chan, C. H., Yusoff, R., Ngoh, G. C., & Kung, F. W. L. (2011). Microwave-assisted extractions of active ingredients from plants. *Journal of Chromatography A*, 1218(37), 6213-6225. <https://doi.org/10.1016/j.chroma.2011.07.040>.
- Hazewindus, M., Haenen, G. R. M. M., Weseler, A. R., & Bast, A. (2012). The anti-inflammatory effect of lycopene complements the anti-oxidant action of ascorbic acid and α -tocopherol. *Food Chemistry*, 132(2), 954-958. <https://doi.org/10.1016/j.foodchem.2011.11.075>.
- Imran, M., Ghorat, F., Ul-haq, I., Ur-rehman, H., Aslam, F., Heydari, M., Shariati, M. A., Okuskhanova, E., Yessimbekov, Z., Thiruvengadam, M., Hashempur, M. H., & Rebezov, M. (2020). Lycopene as a natural antioxidant used to prevent human health disorders. *Antioxidants*, 9(8). <https://doi.org/10.3390/antiox9080706>.
- Kehili, M., Sayadi, S., Frikha, F., Zammel, A., & Allouche, N. (2019). Optimization of lycopene extraction from tomato peels industrial by-product using maceration in refined olive oil. *Food and Bioproducts Processing*, 117, 321-328. <https://doi.org/10.1016/j.fbp.2019.08.004>.
- Khan, U. M., Sevindik, M., Zarrabi, A., Nami, M., Ozdemir, B., Kaplan, D. N., Selamoglu, Z., Hasan, M., Kumar, M., Alshehri, M. M., & Sharifi-Rad, J. (2021). Lycopene: Food Sources, Biological Activities, and Human Health Benefits. *Oxidative Medicine and Cellular Longevity*, 2021. <https://doi.org/10.1155/2021/2713511>.
- Laranjeira, T., Costa, A., Faria-Silva, C., Ribeiro, D., Ferreira de Oliveira, J. M. P., Simões, S., & Ascenso, A. (2022). Sustainable Valorization of Tomato By-Products to Obtain Bioactive Compounds: Their Potential in Inflammation and Cancer Management. *Molecules*, 27(5). <https://doi.org/10.3390/molecules27051701>.
- Lianfu, Z., & Zelong, L. (2008). Optimization and comparison of ultrasound/microwave assisted extraction (UMAE) and ultrasonic assisted extraction (UAE) of lycopene from tomatoes. *Ultrasonics Sonochemistry*, 15(5), 731-737. <https://doi.org/10.1016/j.ultsonch.2007.12.001>.
- Messinese, E., Pitirollo, O., Grimaldi, M., Milanese, D., Sciancalepore, C., & Cavazza, A. (2023). By-Products as Sustainable Source of Bioactive Compounds for Potential Application in the Field of Food and New Materials for Packaging Development. *Food and Bioprocess Technology*. <https://doi.org/10.1007/s11947-023-03158-2>.
- Pengdee, C., Sritularak, B., & Putalun, W. (2020). Optimization of microwave-assisted extraction of phenolic compounds in *Dendrobium formosum* Roxb. ex Lindl. and glucose uptake activity. *South African Journal of Botany*, 132, 423-431. <https://doi.org/10.1016/j.sajb.2020.06.009>.
- Rahimi, S., & Mikani, M. (2019). Lycopene green ultrasound-assisted extraction using edible oil accompany with response surface methodology (RSM) optimization performance: Application in tomato processing wastes. *Microchemical Journal*, 146, 1033-1042. <https://doi.org/10.1016/j.microc.2019.02.039>.
- Sadeghi, A., Hakimzadeh, V., & Karimifar, B. (2017). Microwave Assisted Extraction of Bioactive Compounds from Food: A Review. *International Journal of Food Science and Nutrition Engineering*, 7(1), 19-27.
- Sadh, P. K., Duhan, S., & Duhan, J. S. (2018). Agro-industrial wastes and their utilization using solid state fermentation: a review. *Bioresources and Bioprocessing*, 5(1). <https://doi.org/10.1186/s40643-017-0187-z>.
- Shi, J., Wu, Y., Bryan, M., & le Marc, M. (2002). Oxidation and Isomerization of Lycopene under Thermal Treatment and Light Irradiation in Food Processing. *Preventive Nutrition and Food Science*, 7(2). <https://doi.org/10.3746/jfn.2002.7.2.179>.
- Simić, V. M., Rajković, K. M., Stojičević, S. S., Veličković, D. T., Nikolić, N., Lazić, M. L., & Karabegović, I. T. (2016). Optimization of microwave-assisted extraction of total polyphenolic compounds from chokeberries by response surface methodology and artificial neural network. *Separation and Purification Technology*, 160. <https://doi.org/10.1016/j.seppur.2016.01.019>.
- Sinha, K., Chowdhury, S., Saha, P. das, & Datta, S. (2013). Modeling of microwave-assisted extraction of natural dye from seeds of *Bixa orellana* (Annatto) using response surface methodology (RSM) and artificial neural network (ANN). *Industrial Crops and Products*, 41(1). <https://doi.org/10.1016/j.indcrop.2012.04.004>.
- Trombino, S., Cassano, R., Procopio, D., di Gioia, M. L., & Barone, E. (2021). Valorization of tomato waste as a source of carotenoids. *Molecules*, 26(16). <https://doi.org/10.3390/molecules26165062>.
- Walallawita, U. S., Wolber, F. M., Ziv-Gal, A., Kruger, M. C., & Heyes, J. A. (2020). Potential role of lycopene in the prevention of postmenopausal bone loss: Evidence from molecular to clinical studies. *International Journal of Molecular Sciences*, 21(19). <https://doi.org/10.3390/ijms21197119>.
- Xi, J. (2006). Effect of high pressure processing on the extraction of lycopene in tomato paste waste. *Chemical Engineering and Technology*, 29(6). <https://doi.org/10.1002/ceat.200600024>.
- Zuorro, A. (2020). Enhanced lycopene extraction from tomato peels by optimized mixed-polarity solvent mixtures. *Molecules*, 25(9). <https://doi.org/10.3390/molecules25092038>.

Received: September 13, 2023

Accepted: November 19, 2023

