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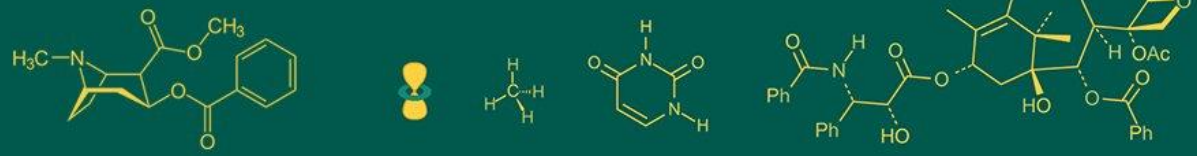

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Multivariate study of process parameters for thermal processing of watermelon juice in a double pipe heat exchanger with phase change material

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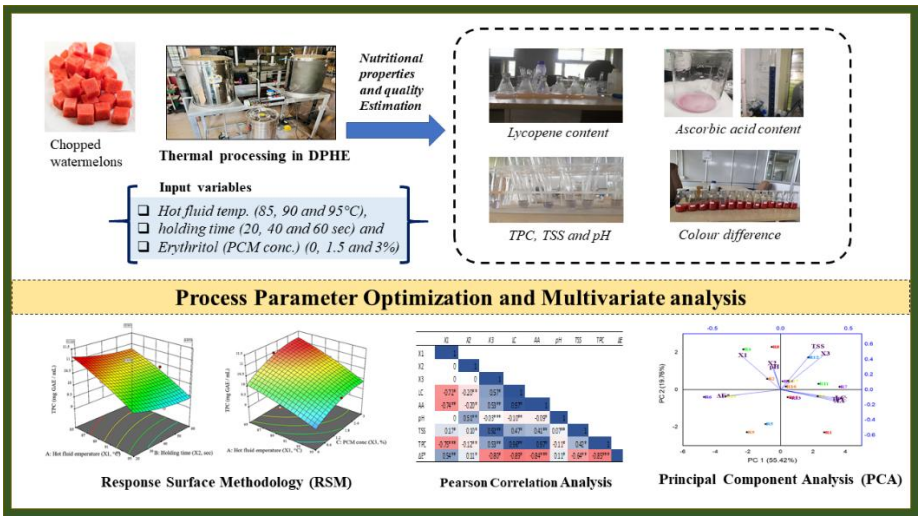
Abstract
Erythritol, a heat-stable natural sugar substitute, is extensively used as a phase change material (PCM) to enhance heat transfer efficiency and prevent thermal degradation of food. This study aims to give thermal treatment on watermelon juice using an erythritol and water mixture in a double-pipe heat exchanger in place of base fluid. The thermal processing parameters were varied as: temperature of hot liquid (85, 90 and 95 °C), holding time (20, 40 and 60 sec) and PCM concentration (0, 1.5 and 3%). The multivariate analysis and optimization using RSM with BBD model were carried out to evaluate the impact on lycopene retention (LC), ascorbic acid retention (AA), color difference (ΔE*), TPC, TSS, and pH. The LC and AA retention increased to 92.3% and 68.12%, respectively, with 3% PCM concentration at 85 °C for 20 seconds. However, pH, TPC, and TSS did not change significantly with an increase in the PCM concentration. In Pearson's correlation matrix, nutritional compounds (TPC, LC, AA) showed strong negative correlations with hot fluid temperature (r=-0.72 to-0.75, $p \leq 0.01$) and ΔE* (r=-0.84 to-0.89, $p \leq 0.01$). PCA explained about 75.18% of variability (PC1: 55.42%, PC2: 19.76%). The optimal thermal processing conditions for watermelon juice were found at 85.79 °C, 20s holding time, and 3% PCM that yield lycopene retention of 71.11 mg/kg, ascorbic acid 5.41 mg/100ml, TSS of 9.2°Brix, and TPC of 10.7 mg GAE/ml. This study highlights the promising potential of PCM in nutrient retention and color preservation during the thermal processing of watermelon juice.

Keywords: Phase change material, erythritol, double pipe heat exchanger, watermelon juice, nutritional properties, multivariate analysis

Introduction
Watermelon (*Citrullus lanatus*) is considered one of the most extensively grown fruits in the world, particularly produced in large quantities in nations like China, India, Turkey, and Brazil. India is one of the leading manufacturers, making a significant contribution to the world market. In 2021, the world produced over 100 million metric tons of watermelon, with India contributing over 2.5 million metric tons [1]. The hydration qualities and rich nutritional profile of watermelon juice, which includes bioactive substances including lycopene (11.3±0.1 mg/100 g), vitamin C (4.5-10.1 mg/100 g), polyphenols (110.0±1.9 mg GAE/100 g), and flavonoids (14.1±0.2 mg QUE/100 g), make it a highly prized beverage [1, 2]. The strong antioxidant lycopene, which gives the skin its red shade, has been connected to several health advantages, such as a lower risk of heart disease and some types of cancer [3]. Essential elements like potassium and magnesium, which support heart health and electrolyte balance, are also abundant in the fruit [3]. Watermelon juice has a short shelf life because of its high water content and perishable nature; hence, preservation methods are needed to maintain its quality and increase storage stability [3-5].
Thermal processing, which includes pasteurization, is one of the best ways to make sure that fruit juices are safe from microbes and to extend their shelf life. High-temperature, short-time (HTST) pasteurization is often used to make fruit juice. This involves heating the juice at 76.6-87.7 °C for 25-30 seconds [4, 6]. Excessive heat exposure, however, can cause the breakdown of volatile molecules that give food their flavour and aroma as well as the substantial loss of heat-sensitive proteins, bioactives including vitamin C, lycopene, and polyphenols [4, 7, 8].

Studies show that long-term heat treatments change physicochemical properties such as pH, total soluble solids (TSS), color, and antioxidant activity. The challenge lies in balancing microbial safety with the preservation of nutritional and sensory attributes [4,6,9,10]. Heat treatment may result in unfavourable off-flavours and irreversible changes in juice texture; therefore, alternate methods that maximize thermal processing efficacy while reducing quality degradation are need of the hour.



Erythritol is a naturally occurring sugar alcohol that is very stable at high temperatures and has shown a lot of promise as a phase change material (PCM) in food processing [11,12]. PCMs are materials that can absorb and release thermal energy during phase changes. This makes it easier to control the temperature when heating and cooling. It is well known that erythritol can improve heat transfer efficiency without compromising product quality [12]. By protecting bioactive chemicals and minimizing thermal degradation, recent research has shown how effective it is in enhancing the thermal processing of fruit juices, including pomegranate and orange juice [13,14]. According to research, erythritol-based PCM mixes help to minimize color and sensory alterations while improving the retention of ascorbic acid, polyphenols, and anthocyanins [11]. The use of erythritol-based PCMs has not been thoroughly investigated in the thermal processing of watermelon juice, which is extremely vulnerable to heat-induced quality loss despite its potential. The application of erythritol-based PCMs for watermelon juice thermal processing optimization represents a substantial research area. Improving the efficiency of heat transfer has been the focus of earlier research, but there haven't been any thorough studies that look at how it affects important nutritional and sensory qualities.

This study aims to fill in that gap by looking at how to improve the thermal processing parameters for watermelon juice using a PCM mixture of erythritol and water in a double-pipe heat exchanger. The purpose of this study is to assess how different thermal processing factors, such as hot fluid temperature (85-95 °C), holding duration (20-60 s), and PCM concentration (0-3%), affect important quality characteristics of watermelon juice, such as color stability, TPC, TSS, pH, and the preservation of lycopene and ascorbic acid. It looks for ideal circumstances that minimize quality loss and increase nutrient retention. Furthermore, multivariate analysis will investigate the relationships between nutritional qualities and processing characteristics. The result thus, will aid in developing a sustainable and effective substitute for traditional pasteurization techniques by incorporating erythritol-based PCMs into thermal processing.

Materials and Methods

Fresh watermelons were bought from the market of Pant Nagar, Uttarakhand. The watermelons were washed, peeled, and chopped into pieces. The pulp was crushed, and the juice was strained through a muslin cloth to separate the seeds, and hence, the juice was smooth. Erythritol, containing 99% purity, was purchased from RAS Green Sweeteners, Pune, and was mixed with water at concentrations of 0%, 1.5%, and 3% W/V. A double-pipe heat exchanger, having concentric pipes in a counter-current configuration, was used for the thermal processing. The system consists of three reservoirs, one for unprocessed watermelon juice and another for processed juice, whereas the third is provided with 2 kW immersion heaters to heat the fluid. The flow loops are used and circulated fluids to avoid direct contact with the juice. The heat exchange took place through stainless steel pipes SS304 of certain specified dimensions for both inner and outer pipes.

Thermal Processing System

Watermelon juice was thermally processed in a double-pipe heat exchanger with counter-current flow at different temperatures (85, 90, 95 °C), times (20, 40, 60 sec), and erythritol concentrations (0%, 1.5%, 3%). The process was done by filling the cold fluid tank with juice and the hot fluid tank with an erythritol-water mixture, heated by a 2-kW rod heater. Fluid flow rates were maintained at 10 L/min for juice and 15 L/min for the hot fluid. Heat transfer occurred through the pipe walls, which were monitored using J and K-type thermocouples. Post-processing, heat transfer coefficient and juice quality parameters lycopene, ascorbic acid, colour, TPC, pH, TSS were evaluated.

Lycopene determination

To each flask, 5 ml of 95% ethanol, 5 ml of acetone with 0.05% BHT, and 10 ml of hexane were added, then 0.6 g of watermelon juice. The mixture was shaken for 15 minutes, and then 3 ml of distilled water was added and shaken again for 5 minutes. The upper hexane layer was then measured at 503 nm by spectrophotometer after 5 minutes at room

temperature, using hexane as a blank. Lycopene content was calculated using the Eqn. (1) [15],

$$\text{Lycopene (mg/gm juice)} = \frac{A_{503} \times 31.2}{\text{gm juice}} \quad (1)$$

Where A_{503} is the absorbance of the hexane phase at 503 nm, 31.2 refers to the molar extinction coefficient, lycopene retention will be calculated using Eqn. (2):

$$\text{Retention}(\%) = \frac{\text{mg lycopene/kg juice after treatment}}{\text{mg lycopene/kg juice before treatment}} \times 100 \quad (2)$$

Ascorbic acid (vitamin C) content

The content of vitamin C in watermelon juice was determined by the indophenols method as described by [16]. Titrant preparation: 50 mg of 2, 6-dichloroindophenol sodium salt and 42 mg of sodium bicarbonate were dissolved in 50 mL of water and diluted with 200 mL of distilled water. The extraction solution was prepared by the dissolution of 15 g metaphosphoric acid and 40 mL acetic acid in 500 mL water. Storage was done at 4 °C. To make the titration, 10 mL of juice from watermelon was mixed with 90 mL of the extraction solution. This was titrated with the titrant until it became bright pink and stayed the same for 5 seconds. Vitamin C retention was calculated using the following Eqn. (3)

$$\text{Retention (\%)} = \frac{\text{mg ascorbic acid/100ml juice after treatment}}{\text{mg ascorbic acid/100ml juice before treatment}} \times 100 \quad (3)$$

Total soluble solids (TSS) and pH

The total soluble solids (TSS) of watermelon juice before and after thermal treatment were determined using a digital hand refractometer (MSW-503 MAC). The sample, 2-3 drops, was positioned on the prism to determine TSS in °Bx. pH was assayed using a digital pH meter, Citizen ID 50-01, by placing the probe in 20 mL of juice at room temperature, provided that the meter had been previously calibrated with pH 4.0 and 7.0 buffer solutions [17].

Total Phenolic Content (TPC)

The total phenolic content of watermelon juice was assayed using the method as described by [18] with some modifications. The juice (100 µL) was added to the distilled water (1500 µL), FCR (100 µL), shaken, and allowed to stand for 3 minutes. 20% sodium carbonate solution (300 µL) was added, and the solution was allowed to turn blue-black; absorbance at 760 nm was determined using a 2 ml cuvette. The blank was prepared with distilled water, FCR, and sodium carbonate. Based on the absorbance, TPC was then expressed in terms of mg GAE/ml.

Colour difference

The colour parameters L* brightness, a* red-green, and b* yellow-blue of watermelon juice samples were determined using a colorimeter (Konica Minolta Chroma Meter CR-400, Japan). The total colour difference ΔE* was calculated as a measure of the overall change in colour in comparison to both unpasteurized and conventionally pasteurized samples according to [19].

$$\Delta L* = (L_1* - L_0*)$$
$$\Delta a* = (a_1* - a_0*)$$
$$\Delta b* = (b_1* - b_0*)$$

After calculating $\Delta L*, \Delta a*, \Delta b*$, the colour difference of each sample was codetermined by using the Eqn. (4)

$$\Delta E* = \sqrt{(\Delta L*)^2 - (\Delta a*)^2 + (\Delta b*)^2} \quad (4)$$

Subscripts '0' and '1' depicted color values for the raw and processed watermelon juices, respectively.

Design of the experiment

Watermelon juice was treated at 85, 90, and 95 °C for 20, 40, and 60 seconds, with PCM concentrations of 0%, 1.5%, and 3%. Response surface methodology (RSM) and Box-Behnken design (BBD) were applied to analyze the effect of variables on responses at a 0.05 probability level, while regression analysis was done using Design-Expert 13. [20] reported that light thermal treatment can preserve lycopene and enhance its bioavailability by releasing plant compounds. However, lycopene content in fruit juices decreases with higher temperatures or longer processing times, depending on the method, temperature, and duration [21].

The experiments were performed according to the BBD design with 3 factors and 3 coded levels, which generates a total of 17 possible experimental runs. RSM was conducted with the main objective to optimize responses such as Lycopene retention, ascorbic acid and change in color (ΔE*) etc. concerning independent variables as hot fluid temperature(°C) (X_1), holding time (s) (X_2) and PCM Concentration (%) (X_3) as depicted in Table 1. The subsequent fitting of experimental data and the correlation between responses (Y) and the independent process parameters is described using the following second-order polynomial function [22]:

$$Y = f(X_1, X_2, X_3, \ldots\ldots\ldots\ldots X_n) + \varepsilon \quad (5)$$

Where,
F = real response function,
ε = residual error
To determine if there exists a relationship between dependent and independent variables, the model development was done using response surface methodology (RSM) through Design Expert 13. Each response was represented by a mathematical equation that correlates with the response surfaces. The response was then expressed as a second order polynomial equation (6) as given by [23].

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{n} \beta_{ii} X_i^2 \quad (6)$$

Where,
B_0, βi, βii, βij = regression coefficients
Xi, Xj = independent variables (where, i = 1, 2,.....n and j = 1,2……n)
n = number of independent variables (n = 3)
Y = response

The model developed for each determination was then examined for lack of fit and significance, while response surface graphs were plotted after removing non-significant terms

Table 1: Actual levels at coded factor levels of independent variables used in the RSM

Symbol	Independent variable	Actual levels at coded factor levels		
		-1	0	1
X_1	Hot fluid temperature (°C)	85	90	95
X_2	Holding time (s)	20	40	60
X_3	PCM Concentration (%)	0	1.5	3

Statistical analysis

All the experiments were performed in triplicate. The RSM-based optimization for the thermal processing parameters was carried out using Design Expert 13 (Stat-Ease Inc., Minneapolis, MN, USA). Furthermore, principal component analysis (PCA) and Correlation analysis were performed using Origin Pro 2018 (OriginLab, USA) software to investigate the optimized conditions.

Results and Discussion

Table 2 shows the experimental design chart of the total 17 runs considered for optimizing the different parameters for thermal processing. Table 3 presents the coefficients of regression and statistical factors corresponding to the input factors and responses of the BBD model, along with the ANOVA of the experimental data.

Table 2 BBD and response of different parameters at different thermal conditions

Exp. No.	X_1 (°C)	X_2 (Sec)	X_3 (%)	Lycopene content (mg/kg)	ascorbic acid (mg/100 mL)	pH	TSS (°BRIX)	TPC (mg GAE/mL)	ΔE*
1	85	20	1.5	71.8	5.4432	5.49	9.1	10.74	2.75793
2	95	20	1.5	67.314	5.0706	5.55	9.18	9.855	5.987
3	85	60	1.5	71	5.3865	5.57	9.14	11	3.585
4	95	60	1.5	64.818	4.86	5.58	9.1754	9.3	6
5	85	40	0	67.86	5.103	5.59	9	9.9	5.4
6	95	40	0	61.59	4.779	5.55	9	9	8.45
7	85	40	3	72	5.518	5.56	9.2	10.8	2.30929
8	95	40	3	65.832	4.8924	5.53	9.23	9.525	3.875
9	90	20	0	66.378	4.99	5.5	9.01	9.6	6.73621
10	90	60	0	63.5	4.8195	5.55	9.05	9.42	7.77777
11	90	20	3	70	5.3298	5.53	9.21	10.62	3.345
12	90	60	3	69.7	5.265	5.56	9.22	10.35	3.54859
13	90	40	1.5	68.64	5.2569	5.51	9.14	10.3	4.789
14	90	40	1.5	68.8	5.2002	5.591	9.15	9.97	5.0078
15	90	40	1.5	69.03	5.184	5.49	9.16	10.11	4.987
16	90	40	1.5	68.54	5.2	5.55	9.17	10.215	5.35082
17	90	40	1.5	69.108	5.2407	5.58	9.18	10.155	5.29

X_1: hot fluid temperature (°C), X_2: holding time (sec), X_3: PCM conc. (%)

Table 3 Regression coefficients and statistical factors for the experimental design model

Coefficients	Lycopene	Ascorbic acid	pH	TSS	TPC	ΔE*
β_0	68.82	5.22	5.56	9.16	10.15	5.085
β_1	-2.89[a]	-0.23[a]	7.45e-16[NS]	0.02[b]	-0.565[a]	1.28[a]
β_2	-0.81[a]	-0.06[a]	0.008[a]	0.011[NS]	-0.19[a]	0.26[b]
β_3	2.28[a]	0.16[a]	0.04[a]	0.1[a]	0.42[a]	-1.91[a]
$\beta_1\beta_2$	-0.42[b]	-0.04[NS]	-1.48e-15[NS]	-0.011[NS]	-0.014[NS]	-0.204[NS]
$\beta_1\beta_3$	0.03[NS]	-0.08[a]	0.005[NS]	0.008[NS]	-0.09[NS]	-0.371[b]
$\beta_2\beta_3$	0.64[a]	0.03[NS]	-0.002[NS]	-0.008[NS]	-0.02[NS]	-0.209[NS]
β_{11}	-0.33[c]	-0.03[NS]	-0.01[b]	-0.013[NS]	-0.089[NS]	-0.42[a]
β_{22}	0.24[NS]	0.001[NS]	-0.008[b]	0.002[NS]	0.102[NS]	-0.08[NS]
β_{33}	-1.67[a]	-0.12[a]	-0.008[b]	-0.04[a]	-0.26[a]	0.35[b]
Model (F-value)	112.08	47.73	44.56	29.97	25.00	94.96
R^2	0.9931	0.9840	0.9828	0.9747	0.9698	0.9919
Adj. R^2	0.9842	0.9634	0.9608	0.9422	0.9310	0.9814
C.V. (%)	0.5246	0.8209	0.1181	0.2022	1.43	4.58

β_1 β_2 and β_3 represents the coefficients of X_1, X_2 and X_3, respectively, whereas β_0 is the intercept of the eqs. NS: not significant ($p>0.1$), [a]Highly significant ($p<0.01$), [b]Moderately significant ($0.01<p<0.05$), [c]Significant ($0.05<p<0.1$).

Effect of thermal processing on lycopene content (LC) of watermelon juice

The combined effect of hot fluid temperature and holding time on lycopene retention in processed juice at the center point of 1.5% PCM conc. Is shown in Fig. 1. It exhibits that at the lowest level of hot fluid temperature and holding time, lycopene retention was maximum. However, by increasing hot fluid temperature from 85 to 95 °C and holding time from 20 to 60 s, there was a decrease in lycopene retention from 71.88 to 64.85mg/kg. This result is due to higher processing temperature and holding time. Combined effect of hot fluid temperature and PCM concentration. On lycopene retention in processed juice is shown in Fig. 1. It is clear from the figure that for all ranges of hot fluid temperature, lycopene retention of processed juice decreases from 71.90 to 61.99mg/kg with a decrease in PCM conc. The graph shows that lycopene retention is at its maximum when the hot fluid temperature is the lowest and the PCM concentration is the highest. Conversely, the minimum lycopene retention occurs when the hot fluid temperature is at its highest and the PCM concentration is at its lowest, as indicated in the figure. Concentration had a more considerable influence on lycopene content than holding time, and higher lycopene content was maintained at higher PCM concentration due to more rapid heat transfer and lower processing time at this state. The main reasons for lycopene destruction or degradation at higher temperatures are isomerization and oxidation [24]. However, [20] suggested that light thermal treatment can retain lycopene content and improve its bioavailability due to the release of chemical

substances of plants from their matrices, facilitating lycopene extraction. Lycopene content of fruit juices decreases after increasing temperature or time of thermal processing, which depends on processing type, temperature, and duration [21]. The quadratic equation representing the effects of independent variables on the lycopene content is expressed in Eqn. (7).

$$\text{Lycopene content} = 68.82\text{-}2.89\ X_1\text{-}0.81\ X_2 + 2.28\ X_3\text{-}0.42\ X_1 X_2 + 0.64\ X_2 X_3\text{-}0.33\ X_1^2\text{-}1.67\ X_3^2 \quad (7)$$

Effect of thermal processing on ascorbic acid content of watermelon juice

At the interactive level combined effect of hot fluid temperature and PCM conc. On ascorbic acid is shown in Fig 1. In this figure, it was observed that keeping PCM conc. At a low level, with increasing hot fluid temperature and vice-versa, the ascorbic acid retention of juice decreased by 5.088 to 4.77mg/100mL, respectively. On the other hand, ascorbic acid retains maximum at low hot fluid temperature and higher PCM concentration, that is, 5.52 mg/mL, while minimum at higher temperatures and lower PCM conc, that is, 4.77 mg/mL. So, if the temperature and the PCM conc. Then, the ascorbic acid retention decreases. Ascorbic acid is very sensitive to thermal processing and is damaged during processing of variable temperatures and durations. So, thermal processing should be carried out at the lowest temperature and duration to retain maximal rates of vitamin C, and that's why replacing water with PCM conc. was significantly effective in vitamin C retention; in fact, this substitution could reduce durations of thermal processing. According to [25, 26], thermal treatments resulted in a vitamin C drop in tomato juice and orange juice, respectively. The latter decrease is probably on account of the intensive sensitivity of vitamin C to heating procedures; so, the thermal treatment of tomato pulp and juices should be carried out at the minimum duration. The latter study mentioned that lower temperatures during the pulp heating could maintain higher rates of ascorbic acid in tomato juices. The following quadratic Eqn. (8) shows the interactions of different independent variables with the ascorbic acid content of the processed juice.

$$\text{Ascorbic ā content} = 5.22\text{-}0.23\ X_1\text{-}0.06\ X_2 + 0.16\ X_3\text{-}0.08\ X_1 X_3\text{-}0.12\ X_3^2 \quad (8)$$

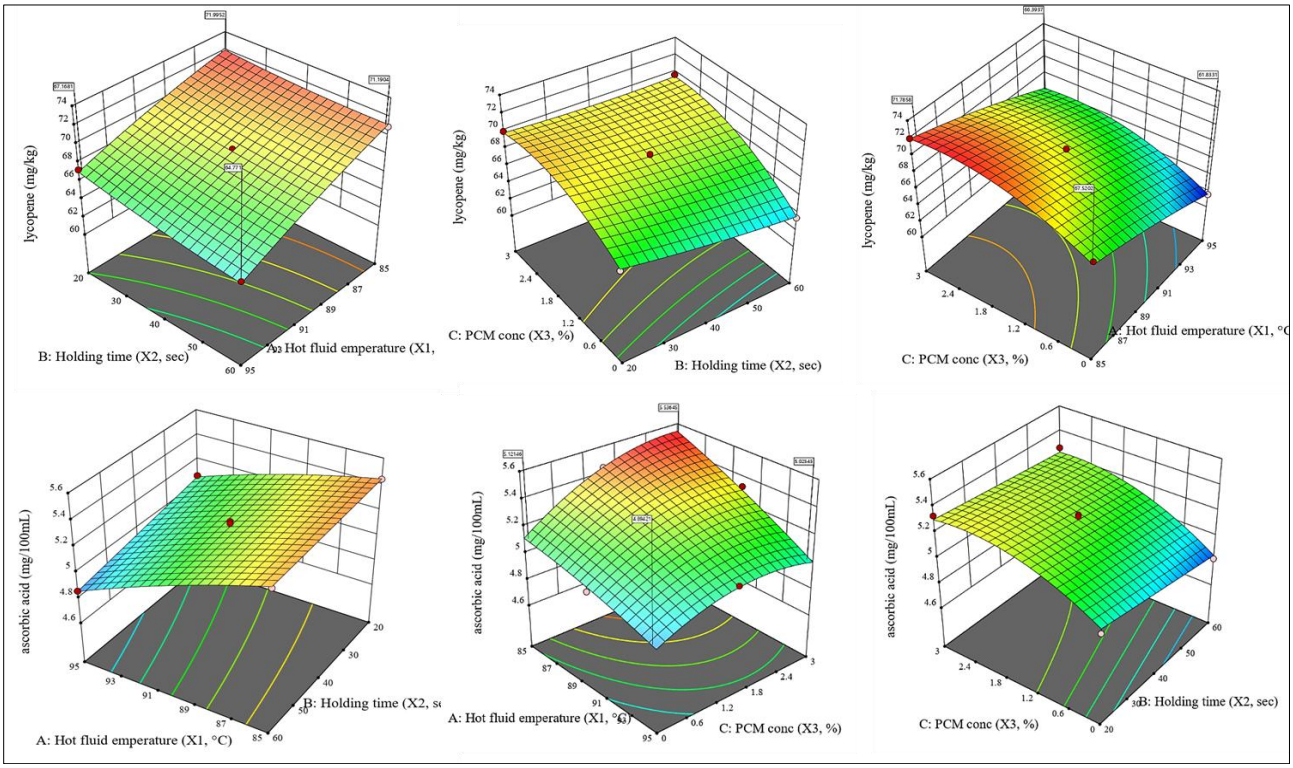


Fig 1: 3D RSM graphs showing the interactions and effects of different thermal processing parameters on (a) Lycopene content; (b) Ascorbic acid content of juice

Effect of thermal processing on pH of watermelon juice

The pH index of watermelon juice was not affected by thermal processing through 1.5 and 3% erythritol water mixture; however, the pH of watermelon juice was a bit lower after thermal processing by water. Generally, the pH was around 5.49-5.59. Similar results were reported by [27] for blended orange-carrot juices processed by Pulsed Electric Fields (PEF). [28] reported insignificant changes in the pH of pasteurized carrot juice. There is only a negligible change in pH during the thermal processing of watermelon juice, and is expressed by the following quadratic Eqn. (9) as:

$$pH = 5.56 + 0.008\ X_2 + 0.04\ X_3\text{-}0.01\ X_1^2\text{-}0.008\ X_2^2\text{-}0.008\ X_3^2 \quad (9)$$

Effect of thermal processing on TSS of watermelon juice

TSS or sugar percentage is used for indicating the percentage of total soluble solids and is one of the important factors in grading the quality of fruit juices [29]**.** Our results illustrate that the impact of hot fluid temperature on the TSS in processed juice suggests that the TSS in processed juice increases from 9.13 to 9.15°BRIX as the hot fluid temperature increases at the center points. Similarly, the TSS in processed juice increases from 9.02 to 9.2°BRIX as

the PCM conc. increases at the center point. A similar parallel study on tomato juice indicated that the pH and TSS indices of tomato juice were not affected by Nano fluid thermal processing significantly, confirming the results of this research [30]. There is only a negligible change in TSS during the thermal processing of watermelon juice, and is expressed as:

$$TSS = 9.16 + 0.02\ X_1 + 0.1\ X_3 - 0.04\ X_3^2 \quad (10)$$

In general, TSS was in the range of 9.1-9.2. The results were in agreement with the reports of [27] for blended orange-carrot juices produced by PEF, where TSS changes were trivial and insignificant.

Effect of thermal processing on TPC of watermelon juice

At the interactive level combined effect of hot fluid temperature and holding time on TPC is shown in Fig. 2. In this figure, it was observed that by keeping the temperature at a low level with increasing holding time and vice-versa, the TPC retention of juice decreased by 11.13 to 10.78 mgGAE/mL, respectively. On the other hand, TPC retains maximum at low hot fluid temperature and low holding time that is 11.14 mgGAE/mL while minimum at higher temperature and higher holding time that is 9.47 mgGAE/mL. So, if the temperature and holding time then the TPC decrease. Indeed, it can be stated that lower temperatures and shorter processing times, along with higher PCM concentrations, have the potential to maintain higher rates of Total Phenolic Content (TPC). The prime reason for phenolic compounds' destruction could be the role of peroxidase in oxidative destruction of phenolic compounds [31]. [32] reported that as a consequence of antioxidants' sensitivity to the temperature, the total phenolic content of the grapefruit juices decreased during conventional and microwave pasteurization; the TPC preservation rate was 75 and 82% for frozen conventional and frozen microwave pasteurized juices. The model quadratic equation representing the effects of the thermal process parameters on TPC with significance ($p<0.05$) is expressed in Eqn. (11):

$$TPC = 10.15 - 0.565\ X_1 - 0.19\ X_2 + 0.42\ X_3 - 0.26\ X_3^2 \quad (11)$$

Effect of thermal processing on color difference of watermelon juice

The combined effect of hot fluid temperature and PCM concentration on color difference in processed juice at the center point of holding time (40s) is shown in Fig. 2. It exhibits that at the lowest level of hot fluid temperature and highest level of PCM concentration, color difference was minimum. However, by increasing the hot fluid temperature from 85 to 95 °C and decreasing the PCM concentration from 3 to 0%, there was an increase in color difference from 4.036 to 5.39. This result is due to higher processing temperatures and lower PCM concentration. The maximum color difference is at the maximum temperature in minimum PCM concentration, while the minimum color difference was at minimum temperature and maximum PCM conc. At center point value that is 40s holding time. The increase in color difference is attributed to changes in the L*, a*, and b* values as temperature and holding time increase while PCM concentration decreases. [33] reported that b* of orange juice processed with thermal operation (90 °C for 20 s) was considerably higher than that of raw fruit juice. Based on reports by [34], b* and a* parameters of orange juice increased and decreased after thermal processing (90 °C for 30 s). The regression model as described by Eqn. (12) showed a significant ($p<0.05$) linear, interactive, and quadratic effect of different thermal processing parameters on the color difference of the juice.

$$\Delta E^* = 5.085 + 1.28\ X_1 + 0.26\ X_2 - 1.91\ X_3 - 0.371\ X_1\ X_3 - 0.42\ X_1^2 + 0.35\ X_3^2 \quad (12)$$

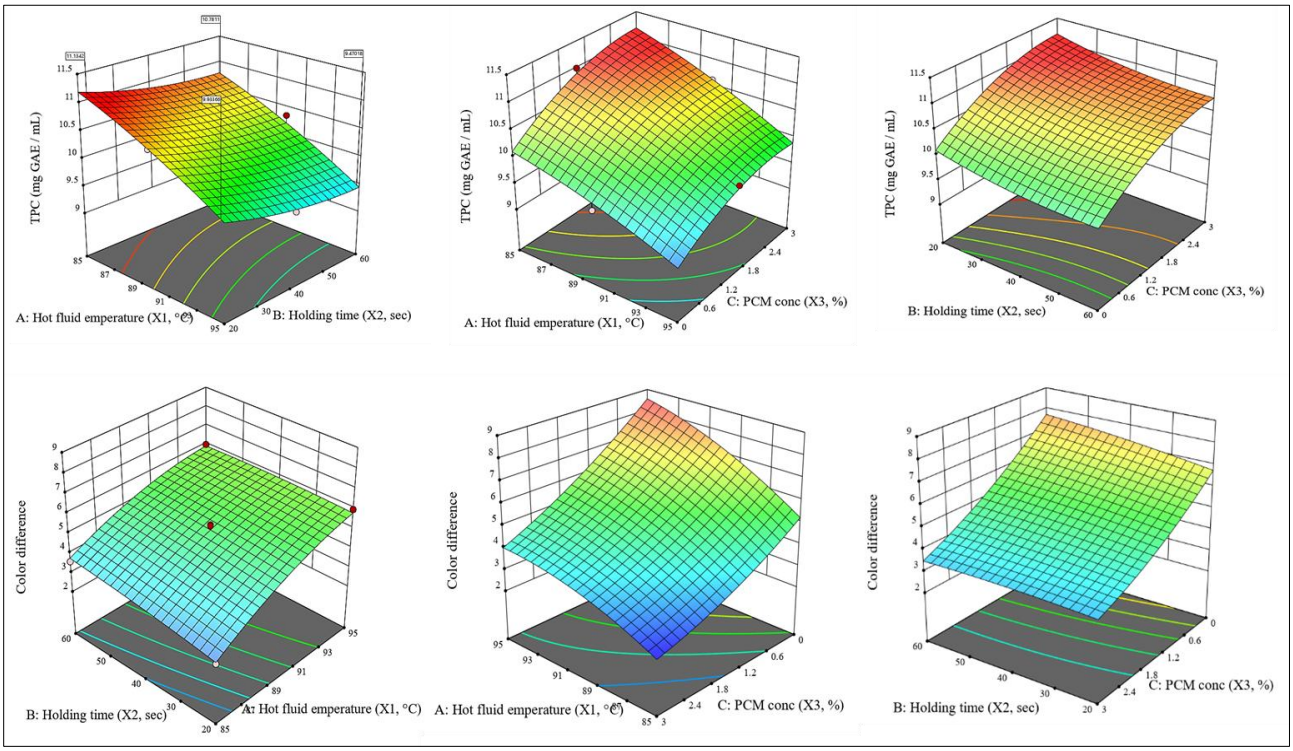


Fig 2: 3D RSM graphs showing the interactions and effects of different thermal processing parameters on (a) TPC and (b) color difference of processed juice

Multivariate analysis

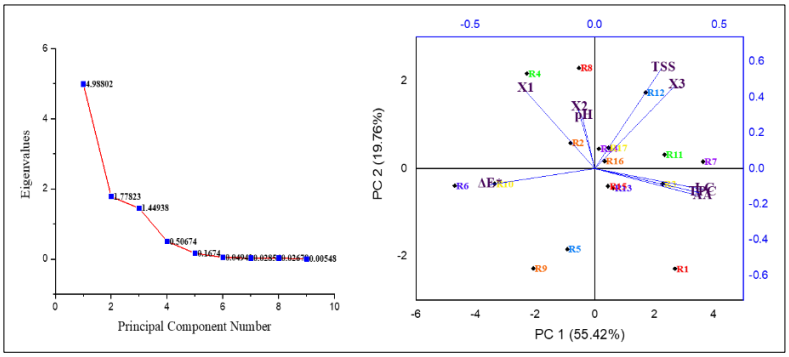
Correlation analysis

Fig. 3(a) presents the correlation matrix containing Pearson's correlation coefficient (r). The values of r assess the degree of association/interaction between various pairs of independent variables and responses. Correlation analysis of the thermal processing parameters and the responses data displayed a moderate positive correlation of hot fluid temperature (X_1) with ΔE* (r=0.54), followed by TSS (r=0.17), while X_1 showed no correlation with pH. Moreover, strong negative correlations were shown by X_1 with TPC (r=-0.75, $p \leq 0.01$), AA (r=-0.74, $p \leq 0.05$), and LC (r=-0.72, $p \leq 0.1$). PCM conc. (X_3) showed a highly strong positive correlation with TSS (r=0.92, $P \leq 0.05$) and a strong negative correlation with ΔE* (r=-0.80, $p \leq 0.1$). Similarly, Lycopene content (LC) exhibited a highly strong positive correlation with AA (r=0.97, $p \leq 0.1$) followed by TPC (r=0.96, $p \leq 0.05$); while a highly strong negative correlation with ΔE* (r=-0.89, $p \leq 0.1$). Also, AA exhibited a strong positive correlation with TPC (r=0.97, $p \leq 0.1$) and a strong negative correlation with ΔE* (r=-0.84, $p \leq 0.01$). All these inter-correlations can be attributed to the fact that the nutritional compounds like lycopene, ascorbic acid and phenols are invariably degraded by the thermal processing quite in the same manner and their thermal sensitivities can be externally assessed by changes/degradation in organoleptic attributes like color, aroma, etc [7, 8, 32]. Furthermore, some highly significant correlations were observed between X_3 and pH (r=-0.03) and TPC and ΔE* (r=-0.85). Overall, the observation aligns with the results reported by Mena *et al*. (2013) [35] in their study on the effect of thermal treatment and blending on the quality of pomegranate juice.

PCA: PCA was performed for the responses of the 17 experimental runs denoted as R1, R2, R3……R17. Fig. 3(b(i)) demonstrates the screen plots depicting eigenvalues and the principal component number, which corresponds to the factor (X_1, X_2 and X_3) and responses (LC, AA, pH, TSS, TPC and ΔE*). Notably, the first three components exhibited eigenvalues greater than 1 (first component: PC1 = 4.98802; second component: PC2 = 1.77823; third component: PC3 = 1.44938). This condition follows the Kaiser-Guttman criterion, stating that only the components with eigenvalues of more than 1 should be considered for further analysis [22]. Adhering to this criterion, the primary two principal components (PC1 and PC2) were chosen to best explain the observed variability. PC1 and PC2 independently accounted for 55.42% and 19.76% with a total of 75.18% of the total variance. Fig. 3(b(ii)) displays PCA bi-plot representing the correlation of response pattern and the connection between different experimental runs in a multidimensional space. It can be observed that the majority of the variables (X_1, X_2, X_3, pH, TSS) positively correlated with PC2, while around 2 variables (TSS and X_3) positively correlated with both PC1 and PC2. On the other hand, ΔE* is negatively correlated with both PC1 and PC2. Moreover, a similar contradictory correlation was also observed between X_1, X_2, pH and TPC, LC, AA where the latter group was found to be positively correlated to PC1 but negatively to PC2, implying that, with enhancement in hot fluid temperature, holding time and pH, the nutritional components like TPC, lycopene retention and ascorbic acid content were inversely influenced. This was in agreement with the findings of [35, 36], who stated that extrinsic factors like time, temperature, pH, and RH significantly affect color, anthocyanin content,% polymeric color, chemical composition (vitamin C, total phenolic content), and enzyme activities during thermal processing.

	X1	*X2*	*X3*	*LC*	*AA*	*pH*	*TSS*	*TPC*	*ΔE**
X1	1								
X2	0	1							
X3	0	0	1						
LC	-0.72*	-0.20**	0.57*	1					
AA	-0.74**	-0.20*	0.53**	0.97*	1				
pH	0	0.51**	-0.03***	-0.10**	-0.09*	1			
TSS	0.17*	0.10*	0.92**	0.47*	0.41**	0.07**	1		
TPC	-0.75***	-0.12**	0.53**	0.96**	0.97*	-0.11*	0.42*	1	
ΔE*	0.54**	0.11*	-0.80*	-0.89*	-0.84***	0.11*	-0.64**	-0.85***	1

(a)



(b(i)) (b(ii))

Fig. 3 (a) Correlation matrix displaying Pearson correlation coefficients among input variables and responses. (statistically difference between the parameters: *** $p \leq 0.01$; ** $p \leq 0.05$ and * $p \leq 0.1$; (b) Principal component analysis of the responses: (i) Eigen value versus PC number scree plot; (ii) PCA biplot representing the distribution of various experimental runs and response variables

Optimization of process parameters

Based on the inference from multivariate analysis, the optimization was performed and achieved by maximizing lycopene retention, ascorbic acid content, TSS, and TPC and minimizing colour difference, while the pH was set in the range between 5.49 and 5.59 as shown in Table 4 with their level of importance. The optimal values for thermal processing parameters were found as: 85.793 °C hot fluid temperature, 20 s holding time, and 3.00% PCM concentration; with a desirability of 0.960. For validation of the predicted values, final runs were conducted with the optimized parameters, and the corresponding responses are listed in Table 5. The relative percentage errors for all the responses were found to be less than 10%. Thus, the regression model established by RSM and BBD was acceptable with 96% desirability.

Table 4: Constraints for optimization and optimized values for thermal processing of watermelon juice

	Name	Goal	Lower Limit	Upper Limit	Imp.	Optimized values
Parameters for optimization	Hot fluid temperature (°C)	is in range	85	95	5	85.793
	Holding time (s)	is in range	20	60	3	20.000
	PCM concentration (%)	is in range	0	3	3	3.000
Responses	Lycopene retention, LC (mg/kg)	maximize	61.59	72	3	71.652
	Ascorbic acid, AA (mg/100mL)	maximize	4.779	5.508	3	5.508
	pH	is in range	5.49	5.591	3	5.568
	TSS(°BRIX)	maximize	9	9.23	3	9.179
	TPC (mg GAE/mL)	maximize	9	11	3	11.110
	Color difference	minimize	2.31	8.45	3	2.152

Table 5: Target values and Fit values of different responses to achieve the optimum conditions

Responses	Predicted values	Actual values	% Error
Lycopene retention(mg/kg)	71.652	71.11	0.76
Ascorbic acid content mg/100mL)	5.508	5.41	1.78
pH	5.568	5.5	1.22
TSS(°BRIX)	9.179	9.2	0.23
TPC (mg GAE/mL)	11.11	10.7	3.69
Colour difference	2.152	2.28	5.95

Conclusion

The incorporation of erythritol significantly reduces the time required for the heating process, especially at higher concentrations, without affecting the quality of juice and its nutrient content. A 3% erythritol-water mixture as partial replacement for water at lower temperatures and shorter holding times resulted in better retention of lycopene, vitamin C, TPC, TSS, and pH, and less color degradation. Lycopene retention in the watermelon juice processed with a 3% erythritol mixture was 92.3%, which was higher compared to the control juice processed with water at the same temperature and duration, standing at 83%. Similarly, retention of ascorbic acid was higher in the 3% erythritol mixture (68.2%) as compared to the water (63%). ΔE* increased with increased temperatures and times; it was the highest value of 5.4 for water at 85 °C for 40 seconds, but the erythritol mixture only reached 2.309 under the same conditions. Minimal pH and TSS changes were noticed after thermal processing with both fluids. Higher concentrations of PCM, lower temperatures, and shorter times also preserved TPC, with the levels reaching up to 10.8 mg GAE/mL. Correlation analysis of the different variables showed that the nutritional compounds (TPC, LC, TSS and AA) exhibited positive correlation among each other (r=0.92 to 0.97, $p \leq 0.1$) and negative correlation with X_1 (r=-0.72 to-0.75, $p \leq 0.01$) and ΔE* (r=-0.84 to-0.89, $p \leq 0.01$). PCA with PC1 and PC2 contributing 55.42% and 19.76%, respectively, with total variability of 75.18%, aptly explains the relative interactions between the variables and the experimental runs. The optimized conditions for the thermal processing of watermelon juice were found at 85.793 °C hot fluid temperature, 20s holding time, and 3% PCM concentration. The optimized parameters yield lycopene retention of 71.11 mg/kg, ascorbic acid 5.41 mg/100ml, TSS of 9.2°Brix, TPC of 10.7 mg GAE/ml, and color difference of 2.28 at pH 5.5. This study presents a new application of erythritol in thermal processing that enhances heat transfer efficiency, reduces processing time, and improves the quality of food products

Author Contribution

Avantika Singh had the idea for the article, performed the data analysis, conducted the experiment, and drafted the manuscript. Raushan Kumar has performed the literature search, manuscript writing, and data analysis. Sachin Kumar has supervised and critically revised the study. Shusheel Bhandari has provided resources, supervised and revised the manuscript. Debapam Saha performed data analysis and manuscript writing. Mrutyunjay Padhiary critically reviewed the paper, supervised and validated the data. Anshu Saxena has conducted the experiments, literature search and data analysis. All authors contributed to the manuscript and approved the final version of the paper.

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Declaration

Conflict of interest: All authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Compliance with ethics requirements: This article does not contain any studies with human or animal subjects.

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