Optimization of process variables for preparation of pomegranate juice-fortified aonla candy

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This study was aimed to evaluate the effect of sugar syrup concentration (SSC) (0, 30 and 60 °Brix (°B)), time of dipping (TD) of aonla segments in pomegranate juice (30, 60 and 90 min) and drying temperature (DT) (50°C, 60°C and 70°C) on the quality of aonla candy. The prepared candy was assessed for its physical, chemical and sensorial characteristics such as total soluble solids (TSS), titratable acidity (TA), ascorbic acid content (AA) and overall acceptability (OAA). Response surface methodology using Box–Behnken design was utilized for formulating the design of experiments, statistical analysis and optimization of process variables. Second-order polynomial models were fitted to determine the responses as a function of process variables. All three independent variables were observed to have significant effect ($P \leq 0.01$) with coefficient of determination ($R^2 \geq 0.90$). The optimum process conditions for preparation of novel aonla candy were SSC of 60°B, TD of 30 min and DT of 70°C. The quality characteristics recorded at optimum experimental condition were TSS of 30.16°B, AA of 207.79 mg/100 g and OAA of 7.71 with lower TA of 1.48%.

Keywords: Aonla candy, pomegranate juice, process variables optimization, response surface methodology,

AONLA or Indian gooseberry (*Emblica officinalis* Gaertn.) is a potential gift of nature to mankind. The semi-arid and arid regions contribute towards ample production of aonla in the country. The fruit is grown commercially because of high economic returns, medicinal and nutraceutical value[1,2]. It is suitable for marginal lands and does not require much care[3]. At present, aonla is being cultivated in an area of about 91,000 ha with an annual production of 0.989 million tonnes in the country[4]. Fruits of aonla are a rich source of vitamin C (400–600 mg/100 g), pectin (2.25%–11.19%)[5] and polyphenols (24.61%–31.12%)[6] which prevent oxidation of vitamin C, and are being used in the Ayurvedic and Unani systems of medicine[7]. Aonla fruits are not consumed as fresh because of their sour and astringent taste. The nutritive and remedial worth offers great potential for its processing into many valorized products like candy, dried powder, juice, preserve, pickle, ready-to-serve beverages, shreds, etc.[8].

Owing to its good keeping quality, aonla candy has considerable demand in domestic as well as international market. Further, to strengthen its demand, retention of quality attributes and its storability are of considerable importance. Aonla candy is usually prepared by dipping in sugar syrup followed by cabinet drying, which results in loss of nutritional quality. Hence, there is need to fortify it with nutrition-rich sweeteners. Therefore, use of pomegranate juice in the preparation of aonla candy will increase its nutritional value as well as colour acceptability. Pomegranates are rich in polyhenols and have high antioxidant capacity which makes it nutritionally important for human health[9]. Pomegranate juice is highly acceptable and makes a delicious drink. It contains sugar (15.2–20.5%), acidity (0.52–1.6), pectin (0.05–1.2%), ascorbic acid (3.3–6.4 mg/100 g) and many minerals[7].

Significant studies have been reported regarding the formulation of aonla candy, but there is none involving preparation of aonla candy by impregnation of pomegranate juice to improve the colour and nutritional quality of the end product. Therefore, the present study was undertaken to assess the nutritional quality of aonla candy fortified with pomegranate juice using response surface methodology (RSM).

Uniformly ripened and mature aonla fruits of cultivar Chakaiya and fresh pomegranate fruits of cultivar Mridula were harvested during January 2017 from the experimental orchard of ICAR-Central Institute of Post-Harvest Engineering and Technology, Abohar, Punjab, India. Fresh aonla fruits of uniform size were selected and washed with tap water. Salt, sugar and other chemicals were procured from the local market of Abohar. Pomegranate fruit was cut in half using stainless-steel knife and arils were removed manually. Arils used to prepare juice were placed into a juice extractor. The washed aonla fruits were blanched in hot water at a temperature of 85°C–90°C for 8–10 min followed by dipping in cold water. Segments were separated manually and dipped in 2.5% salt solution for 24 h at ambient temperature. Thereafter, the segments were taken out and dipped in different concentrations of sugar syrup (0, 30 and 60°Brix (°B)) by maintaining the ratio of sugar syrup to aonla segments as 2 : 1 (v/w). Next the sample was dipped in pomegranate juice for different time periods (30, 60 and 90 min). The pomegranate juice was allowed to drain for 2 min followed by drying of aonla segments at various temperatures (50°C, 60°C and 70°C) till the moisture content of candy reached 11–12% according to the experimental design. It was then packed in airtight plastic jars till the further evaluation.

RSM (Design expert version 9.0, USA) was adopted for optimization of sugar syrup concentration (SSC), time

of dipping (TD) and drying temperature (DT) for the preparation of pomegranate juice-fortified aonla candy. Preliminary trials were conducted in order to identify the range of selected variables (Table 1). The Box–Behnken design was utilized for the experimental design using the range of process variables, i.e. SSC (0, 30 and 60°B), TD (30, 60 and 90 min) and DT (50°C, 60°C and 70°C) (Table 2).

The data obtained for individual responses were fitted in a polynomial equation as given below

$$Y_k = \beta_0 + \sum_{i=1}^{M} \beta_i X_i + \sum_{i=1}^{n}\sum_{j=1}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{m} \beta_{ii} X_i^2, \qquad (1)$$

where Y_k is the response variable, β_0 the value of the fitted response at the centre point of the design, i.e. (0, 0), and β_i, β_{ij}, β_{ii} are the linear, quadratic and interactive regression coefficients respectively. X_i and X_j are the coded independent variables. Corresponding magnitude of the coefficients in the equation represents the effect of a particular parameter on the response.

Standard procedures were employed to determine moisture content (Method 925.10)[10] using a hot-air oven, titratable acidity (Method 942.15)[10] and ascorbic acid content (Method 967.21)[10]. Total soluble solids (TSS) were measured using a hand-held refractometer (M/s Erma, Japan).

The fortified candy samples were organoleptically evaluated by a panel of 20 semi-trained people (age 30 to 40 years) using a nine-point hedonic scale according to the method of Ranganna[11].

RSM was adopted for design of the experiment, while data analysis and regression analysis were used for model fitting[12]. Optimization of multiple responses was achieved by numerical optimization technique, where goals were assigned to the variables (within range) and responses (maximize, minimize, target, within range, none)[13]. Among the solutions obtained, the one having maximum desirability was chosen as the optimal process condition[12]. The
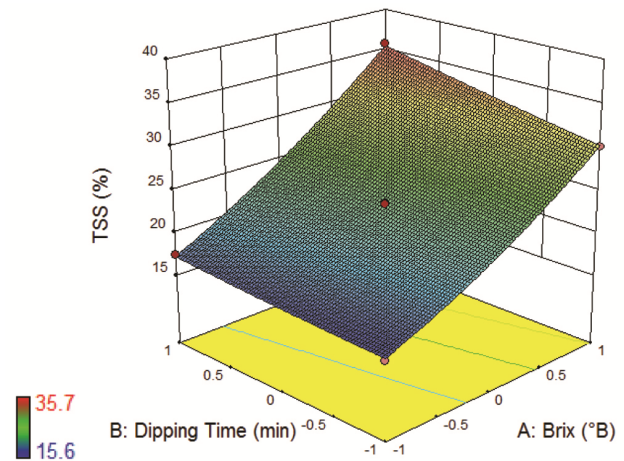

Figure 1. Response surface curve showing variation of total soluble solids (TSS) as a function of time of dipping (TD) and sugar syrup concentration (SSC).

Table 1. Coded and actual levels of process variables

Independent variables	Coded and actual levels		
	−1	0	1
Sugar syrup concentration (SSC), °B (X_1)	0	30	60
Time of dipping (TD), min (X_2)	30	60	90
Drying temperature (DT), °C (X_3)	50	60	70

Table 2. Three level Box–Behnken experimental design with coded and actual values (coded values are given in parenthesis)

Run	SSC (°B)	TD (min)	DT (°C)
1	0 (−1)	30 (−1)	60 (0)
2	60 (1)	30 (−1)	60 (0)
3	0 (−1)	90 (1)	60 (0)
4	60 (1)	90 (1)	60 (0)
5	0 (−1)	60 (0)	50 (−1)
6	60 (1)	60 (0)	50 (−1)
7	0 (−1)	60 (0)	70 (1)
8	60 (1)	60 (0)	70 (1)
9	30 (0)	30 (−1)	50 (−1)
10	30 (0)	90 (1)	50 (−1)
11	30 (0)	30 (−1)	70 (1)
12	30 (0)	90 (1)	70 (1)
13	30 (0)	60 (0)	60 (0)
14	30 (0)	60 (0)	60 (0)
15	30 (0)	60 (0)	60 (0)
16	30 (0)	60 (0)	60 (0)
17	30 (0)	60 (0)	60 (0)

Table 3. Analysis of variance and coefficient estimates of selected quadratic models for responses

Parameter	TSS (°B)	AA (mg/100 g)	TA (%)	OAA
Intercept	23.42	171.98	2.678	7.46
X_1	8.162**	27.375**	−1.255**	0.625**
X_2	1.637**	20.025**	−0.241	0.075**
X_3	−0.05	−1.70**	−0.411**	−1.1E-16
X_1X_2	0.95**	−29.775**	0.617**	−6.7E-16
X_1X_3	−0.075	11.075	−0.127	2.96E-18
X_2X_3	−0.125	−28.975**	0.05	0.05
X_1^2	1.14**	−16.277	0.783**	−0.405**
X_2^2	0.14	9.222	−0.134	0.045
X_3^2	−0.235	−43.727**	0.411**	0.195
ANOVA				
R^2	0.99	0.90	0.96	0.90
Model F-value	679.49**	7.42**	18.57**	7.04**
Lack of fit (P value)	0.09	0.84	0.35	0.61
CV (%)	1.27	13.39	10.75	3.40

P value indicates the level of significance. **refers to significance level of 5%. Intercept refers to the constant for linear and quadratic model. X_1, Sugar syrup concentration; X_2, Time of dipping; X_3, Drying temperature; TSS, Total soluble solids; AA, Ascorbic acid; TA, Titratable acidity; OAA, Overall acceptability. X_1X_2, X_1X_3 and X_2X_3 represent interaction effects of process variables. X_1^2, X_2^2 and X_3^2 represent quadratic effects of process variables.
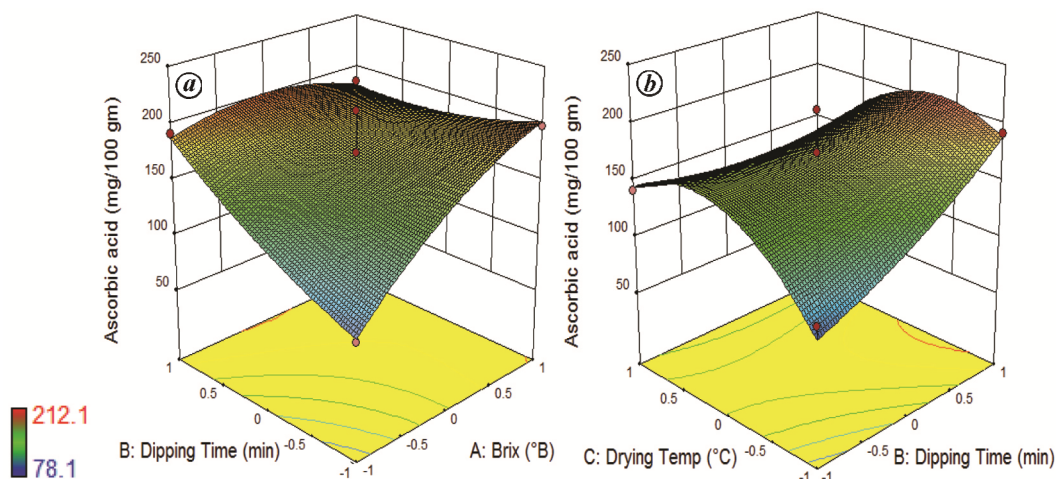
Figure 2. Response surface curve showing variation in ascorbic acid (AA) as a function (*a*) SSC and TD, and (*b*) TD and drying temperature (DT).
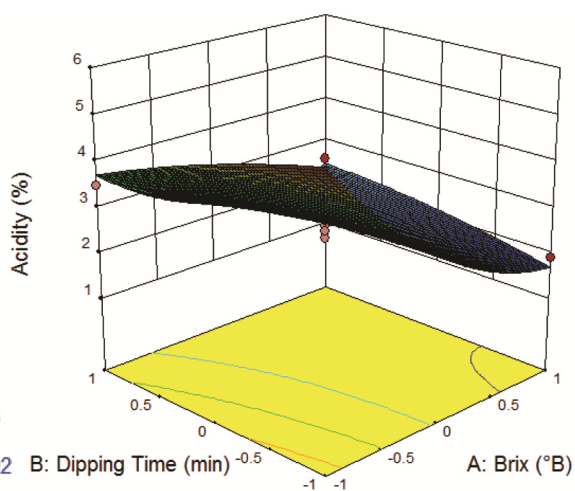

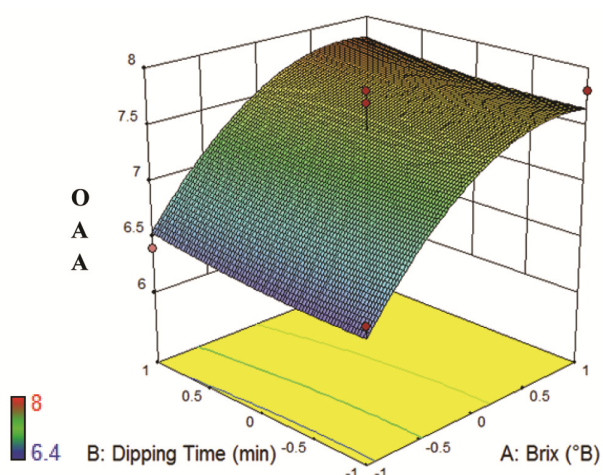**Figure 3.** Response surface plot showing the effect of SSC and TD on titratable acidity (TA).

Figure 4. Response surface curve showing the variation in overall acceptability (OAA) with respect to SSC and TD.

three-dimensional contour graphs were plotted representing the effect of two variables on a particular response.

Table 3 presents the regression coefficients (linear, interactive, quadratic) pertaining to various responses along with their respective levels of significance. Higher coefficient of determination ($R^2 > 0.90$), and model *F*-value substantiated that the models for all responses were significant ($P < 0.01$). Lack of fit of all the models was not significant, which indicates that the models were correlated well with the measured data.

TSS of the pomegranate juice fortified candy was found to be in the range 15.6–35.7%. The effect of linear terms of SSC and TD, interaction effect of SSC and TD and quadratic effect of SSC were significant (Table 3). The increase in SSC from 0 to 30°B led to increase in TSS of fortified candy. However, further increase in SSC (beyond 30°B) showed positive quadratic effect on TSS. Positive linear effect of TD in pomegranate juice was observed from 30 to 90 min of dipping on TSS (Figure 1).

The linear positive terms of SSC and TD indicated that AA increased with increase in SSC and TD in pomegranate juice, whereas decrease in AA was observed with increase in DT (Table 3). The presence of negative interaction terms of SSC and TD as well as TD and DT confirmed that an increase in their levels led to reduced values of AA. Also, AA content of pomegranate juice-fortified aonla candy ranged from 78.1 to 212.1 mg/100 g (Figure 2). The obtained models were found appropriate in predicting the responses, as also evident from the non-significant values of lack of fit. The developed model for ascorbic acid had $R^2 = 0.905$, which indicates that it adequately explains 90.5% of total variation.

TA of the pomegranate juice fortified candy was found to be 1.92–5.6% (Figure 3). Table 3 indicates that TA decreased with increase in SSC, TD and DT. The positive regression coefficients of interactive terms among SSC
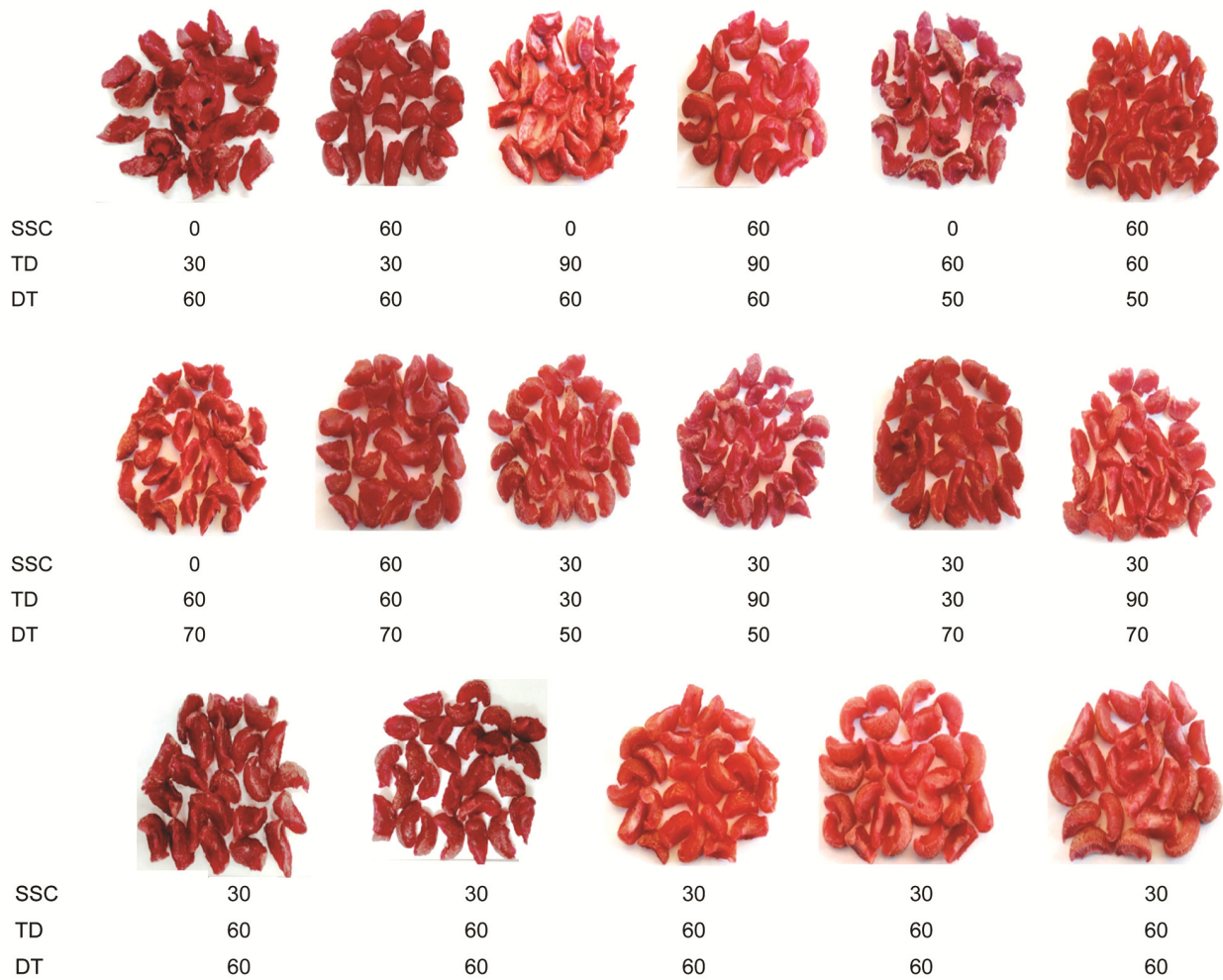
SSC	0	60	0	60	0	60
TD	30	30	90	90	60	60
DT	60	60	60	60	50	50

SSC	0	60	30	30	30	30
TD	60	60	30	90	30	90
DT	70	70	50	50	70	70

SSC	30	30	30	30	30
TD	60	60	60	60	60
DT	60	60	60	60	60

Figure 5. Fortified aonla–pomegranate candy prepared using different process conditions.

and TD showed that they were linearly associated with TA of fortified candy. Similarly, positive linear trend was observed with quadratic coefficients of SSC and DT in relation to TA. The second-order polynomial equation after removing non-significant variables is presented below

$$TA\ (\%) = 2.678 - 1.255X_1 - 0.411X_2 + 0.617X_3 + 0.783X_1^2 + 0.411X_3^2\ (R^2 = 0.96). \qquad (2)$$

The linear positive terms of SSC and TD were observed from 0 to 30°B and from 30 to 90 min respectively, which resulted in increase in OAA of fortified candy with increase in SSC and TD. The negative quadratic coefficients of SSC suggested that further increment in SSC value beyond 30°B resulted in lower OAA score (Table 3). The OAA score of aonla candy ranged from 6.4 to 8 (Figure 4). The highest value for OAA (8.00) was observed at 60°B of SSC, 60 min of TD and 50°C of DT. Figure 5 is a pictorial representation of fortified candy prepared using different process conditions.

Optimization was carried out by applying the following constraints: maximization of TSS, AA, OAA and minimization of TA. Optimum conditions obtained for production of the desired candy were SSC of 60°B, DT of 30 min and DT of 66.85°C–70°C. The corresponding values of responses were: TSS of 30.16°B, AA 207.79 mg/100 g, TA 1.48% and OAA 7.71. The observed values of AA were on par with the sugar-free sucralose aonla candy, whereas TA and OAA values were found to be higher[14]. The high value of TA may be due to the acidic nature of pomegranate juice. Vishen *et al.*[15] prepared flavoured aonla candy using ginger (5%) with TSS 70.32°B, acidity 0.59%, AA 111.75 mg/100 g and OAA 8.78. In another study, aonla candy having TSS 72°B, acidity 0.51%, AA 132.80 mg/100 g and OAA 8.02 was selected for fortification with ginger (2%) extract and the organoleptic properties, viz. flavour (8.75), colour (8.55) and astringency (8.82) were recorded[16].

Pomegranate juice-fortified aonla candy was prepared in this study by optimizing the levels of sugar syrup, dipping time and drying temperature. Statistical analysis

substantiated the suitability of fitted response models and satisfactorily predicted the variation in processing parameters. The optimum process conditions for preparation of novel aonla candy were SSC 60°B, TD 30 min and DT 70°C. The study confirms the feasibility of development of this innovative product with a greater nutritive value, which also may attract more attention in the market.

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Potential application of yellow gypsum from LD slag as a soil conditioner

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In the present study, ICP-AES and ICP-MS techniques were used to analyse and validate the content of heavy and trace elements in yellow gypsum samples produced by a chemical process from a solid waste generated at an integrated steel plant. The present study tries to demonstrate that the content of heavy metals like lead, mercury and arsenic in yellow gypsum is less than the toxicity characteristic leaching procedure (TCLP) norms set for a comparable industrial by-product phospho-gypsum. This study also concludes that yellow gypsum contains some elements (copper, boron, etc.) in traces, apart from heavy metals which are beneficial to plants as micronutrients.

Keywords: Heavy metals, ICP-MS, ICP-AES, trace elements, yellow gypsum.

QUANTIFICATION of hazardous, heavy and trace elements in products, particularly produced from industrial wastes is very important for their possible applications in various sectors especially in agriculture. Efforts are being made worldwide by scientists for economic utilization of steel plant wastes. One such effort is the production of high purity iron and CaO-based sorbent using acetic acid by Tian *et al.*[1] and secondly production of yellow gypsum and gypsum by Ashrit *et al.*[2,3].

Yellow gypsum produced from the Ling-Donawitz (LD) slag fines has very good plant nutrient value in terms of calcium, iron, phosphorus, magnesium and silicon, apart from various other trace elements beneficial for plants like boron, copper, manganese, etc. Environment protection agency (EPA), USA has also studied the quantity of contaminants mainly heavy metals and non-nutrient metals present in various fertilizers as a part of information gathering initiative[4]. Such studies are essential as these contaminants enter the food chain through plants and vegetables. To quantify the heavy and trace elements present in yellow gypsum, sample preparation is an important step of the analysis. Lithium metaborate fusion dissolution method and open acid digestion with different acid combinations followed by inductively coupled plasma-mass spectroscopy (ICP-MS) analysis were discussed by Roy *et al.*[5]. Similarly, Cremer and Schlocker[6] had discussed about lithium borate fusion

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