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Research Paper

Effect of Pre-treatments and Open Sun Drying of Grapes on its Quality

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ABSTRACT

Pre-treatment is a necessary step in raisin production in order to ensure the increased rate of water removal during the drying process. Drying grapes can help preserve it for a longer duration. In present paper, the grapes of Manikchaman variety was treated with Treatment T_1 = 2.5% NaOH for 3 sec followed by 2% KMS for 2 minutes and Treatment T_2 = 2.5% potassium carbonate + 2% ethyl oleate solution for 5 minutes and dried by open sun drying. The drying time for treatment T1 was 85 hrs and the drying rate was 0.1243 g to 7.30×10^{-3} g. The drying data was fitted with various models the Page model, the Lewis model, the Henderson and Pabis model, and the Two-term exponential model. Exponential two terms Logarithmic drying model was well fitted to the experimental data with r^2 = 0.9991 and 0.9947; MSE = 8.481×10^{-5} and 4.996×10^{-5}; χ^2 = 0.0150 and 0.0649 for treatment-1and treatment-2 solution, respectively. Nutritional analysis of fresh ripened grapes and grape raisins has also been determined i.e., Moisture content, TSS, Titrable acidity, pH, Reducing sugar, Total sugar, Non-reducing sugar, Ascorbic acid, color (yellowness index) and Hardness. The moisture content in grape raisins 14.54%, TSS 72.67 °B, Titrable acidity 2.75%, pH 4.77, Reducing sugar 63.10%, Total sugar 65.67 %, Non-reducing sugar 2.67, Ascorbic acid 20.98 mg, yellowness 71.72 and hardness 3.76 for Treatment-1. The sensory score for best Treatment T1 was color 6.75, flavor 7.30, texture 7.37, and taste 7.25.

Keywords: OSD, moisture ratio, drying kinetics, quality parameters

Grapes (*Vitis vinifera* L.) belong to the *Vitaceae* family is believed to have originated in Armenia near the Black and Caspian seas in Russia. Grape production is widespread throughout the world, exceeding 68 million tons (FAOSTAT, 2010). The production of fresh grapes in India is about 26.83 million MT with an area of 1.36 million ha under cultivation. Maharashtra is the leading state, occupying 72.76 percent of the total area of the country with an extent of 1.03 million ha, producing 21.37 million MT of grapes per annum (NHB, 2017).

Currently, chemical pre-treatment methods are used frequently to dissolve the wax layer and accelerate the drying rate (Bingol *et al.* 2012; Doymaz, 2006; Doymaz and Pala, 2002; Esmaiili *et al.* 2007). Chemical pre-treatment consists of dipping grapes into an alkaline solution, i.e. NaOH (Berna *et al.* 1991; Femenia *et al.* 1998; Carranza-Concha *et al.* 2012), or in oil emulsion: ethyl oleate and K_2CO_3 (Cinquanta *et al.* 2002; Doymaz, 2004) for several minutes. By this way, the wax is dissolved, thus reducing the resistance to water diffusion through the peel.

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Dipping in hot water or the use of chemicals such as potassium metabisulphide (KMS), potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), and ethyl or methyl oleate emulsions are some of pre-treatments widely used for fruit drying to increase drying rate and improve the colour quality of products (Mahmutoglu *et al.* 1996; Di Matteo *et al.* 2000; Kingsly *et al.* 2007; Serratosa *et al.* 2008; Bingol *et al.* 2008; Shi *et al.* 2008).

Drying of fruit and vegetable is one of the oldest forms of food preservation methods known to man and is the most important process to preserve food since it has a great effect on the quality of the dried products. The major objective indrying agricultural products is the reduction of the moisture content to a level, which allows safe storage over an extended period.

Various researchers have reported the drying characteristics of the fruits and vegetables by Open-air sun drying. Jain and Tiwari (2003) studied the thermal aspects of open sun drying of various crops green chillies, green pea, white gram (*kabuli chana*), onions, potatoes, and cauliflower; Mahmutoglu *et al.* (1996) studied the sun / open air sun drying of differently treated grapes and storage stability of dried grapes, and Maskan *et al.* (2002) studied the hot air and sun drying of grape leather (pestil). Sun drying is in open air sun and is still practiced in many countries. This method is cheapest and is successfully employed in grapes-producing countries. It is traditionally practiced because there is a negligible cost in processing and work of spreading and turning the crop. In open air sun drying (OSD), the crop is spread in a thin layer on the ground and exposed directly to solar radiation, wind and other conditions. Sun-drying is still the most common method used to preserve agricultural products in most tropical and subtropical countries (Pangavhane and Sawhney, 2002).

The mathematical modelling of the grape drying process is important in understanding the heat and moisture distributions occurring during the production and processing of dried grapes. The accuracy of determination of heat and mass transfer parameters required for modeling of the drying process depends on assumptions made in formulating the model and the solution procedure (Esmaiili *et al.* 2007).

(Doymaz, 2012) reported Midilli *et al*. model showed a better fit with high R^2, and low $\chi 2$ and RMSE values for open air sun drying of grapes. Doymaz and Pala, 2002 and Sawhney *et al.* (1999) found the Page model suitable for air drying of grapes pre-treated with chemical solutions.

In the present study, open sun drying of pre-treated grapes has been carried out. The influence of dipping solutions such as ethyl oleate + potassium carbonate, NaOH and KMS, along with open sun drying, were also studied. Also, the drying time and quality of grape raisins were compared with those pre-treated dipping solutions. Sensory analysis of the dried product has also been carried out.

1. MATERIALS AND METHODS

1.1 Sample preparation

Grapes (*Vitis venifera* L.) of *Manikchaman* variety were purchased from a local market located at the Agricultural Produce Market Committee (APMC), Vashi. Grapes fruits were washed thoroughly under running tap water and weighed, then dipped in two different pre- treatment solutions i.e. Treatment 1 = 2.5% NaOH plus 2% KMS and Treatment 2 = 2.5% potassium carbonate + 2% ethyl oleate solution. Then, the berries are cut from the bunch and separated, and spread on perforated trays.

1.2 Moisture Content

The moisture content of fresh grape sample dried grapes was determined as per AOAC, 2010. The hot air oven calculated initial moisture content of the fresh grape sample and dried grapes at 105 °C ± 1 °C for 24 hours. The final weight of dried grapes were recorded after 24 hours. The moisture content of the fresh grape sample and dried grapes was determined by following formula (Chakraverty, 1994).

$$\text{Moisture content (db)\%} = \frac{W_1 - W_2}{W_2} \times 100 \qquad \ldots(1)$$

Where,

W_1 = Weight of sample before drying, *g*

W_2 = Weight of sample after drying, *g*

1.3(a) Open air sun drying of grape

Firstly, the floor surface where open sun drying is carried out is cleaned. The perforated trays of 81 × 41 × 3.4 cm in length, width and height, respectively, were mounted on galvanized angles. The trays were kept in sunlight at 1.5 feet height above the ground surface for cross-flow air drying, and care was taken that the product should get sunlight throughout the whole day. The pre-treated grapes were placed on the perforated trays of 1x1 mm mesh size for open drying. The observations were recorded i.e. product temperature, ambient air temperature, relative humidity etc. Fig. 1 shows the open-air sun drying of pre-treated grapes with the samples were dried, and also the weight loss of each sample was recorded at regular intervals for 10 min for first 3 h and then after 30 min at each till the moisture 14-15 (% db) was achieved by using electronic weighing balance and drying characteristics were studied. The longitude for Roha is 69° 16′ 14.74′′ E, and Latitude for Roha is 23° 11′14.26′′ N. The experiment was triplicated for each treatment, and corresponding drying characteristics were studied. The experiment was carried out from 4 April 2018 to 15 April 2018 dates.

1.3(b) Open air sun drying parameter measurement

Humidity and ambient air temperature were measured using a digital thermo- hygrometer (Make: Crystal instruments, Mumbai; Model: Temptec) with an accuracy of 1°C and 1% RH. Air velocity of ambient air was measured by anemometer (Make: Lutron Electronics, Taiwan; Model: AM4202) having an accuracy of 0.1 m.s^{-1}. The product temperature measured by inserting the sensors into the product during the drying using a data logger (Make: Ambetronics; Model: TC800D). The initial moisture content, weight loss with respect to time during drying, final moisture content of the grape were also recorded. Drying was carried out for up to 11 days. Three replications were taken for each experimental run.

Fig. 1: Experimental setup for open air sun drying

1.3.1 Moisture ratio

The moisture ratio of grapes was calculated on dry basis using following formula (Chakraverty, 2005).

$$\text{Moisture ratio} = \frac{M - M_e}{M_o - M_e} \qquad \ldots(2)$$

Where,

MR = Moisture ratio

M = Moisture content at any time θ, %(db)

M_e = EMC, % (db)

M_0 = Initial moisture content, %(db)

1.3.2 Drying model

Moisture Content (% db) versus drying time (min) and drying rate (g of water/100g bone dry material/min) with respect to moisture content was determined for drying of grapes. Moisture ratio versus drying time (min) was also determined from the experimental data.

Table 1: Mathematical models tested with the moisture ratio of grapes

Sl. No.	Model	Equation	Reference
1	Newton	MR = exp (-kt)	Westerman *et al.* 1973
2	Page	MR = exp (-kt^n)	Zhang and Litchfield, 1991
3	Modified Page equation-II	MR = a.exp (-kt)^n	Zhang and Litchfield, 1991
4	Exponential	MR = exp (-kt)	Liu and Bakker-Arkema, 1997
5	Henderson and Pabis	MR = a.exp (-kt)	Henderson and Pabis, 1961
6	Logarithmic	MR = a.exp(-kt) + C	Zhu and Shen, 2014
7	Wang and Singh	MR = 1 + at + bt^2	Wang and Singh, 1978
8	Two term	MR = aexp (-k0t) + bexp(-k1t)	Henderson, 1974

Various mathematical models listed in Table 1 were tested on the experimental data on moisture ratio versus drying time in minutes of grapes dried with convective hot air drying. The moisture ratio determines the unaccomplished moisture change, defined as the ratio of the free water still to be removed at time t over the initial total free water (Henderson and Pabis, 1961).

The root mean square error (RMSE) was determined as per equation (3). The model was considered as best fit based on higher r^2 (Corelation coefficient) values, lower MSE, and lower χ^2 (chi-square) value.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{n}\left(MR_{\exp} - MR_{pre}\right)^2\right]^{1/2} \qquad \ldots(3)$$

Where,

MR_{exp} = experimental moisture ratio

MR_{pre} = predicted moisture.

N and *n* are the number of observations and the number of constants respectively (Togrul and Pehlivan, 2003).

1.3.3 Correlation regression coefficient and error analysis

The goodness of fit of the tested mathematical models to the experimental data was evaluated with the higher correlation coefficient (*r^2*), lower chi-square (χ^2), and lower value of RMSE. The higher the r^2 value and the lower the chi-square (χ^2) equation (4) and the lower value of *RMSE* values, the better is the goodness of fit (Ozdemir *et al.* 1999; Ertekin and Yaldiz., 2004; Wang *et al.* 2007). According to Wang *et al.* (2007) reduced chi-square (χ^2) and root mean square error (*RMSE*) can be calculated as follows:

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{\exp,i} - MR_{pre,i}\right)^2}{N - Z} \qquad \ldots(4)$$

Where,

$MR_{exp,i}$ = is the i^{th} experimental moisture ratio,

$MR_{pre,i}$ = is the i^{th} predicted moisture ratio,

N = is the number of observation, and

z = is the number of constant.

The non-linear regression analysis was performed by using the statistical software SAS 6.5.

1.3.4 Effective moisture diffusivity

The effective moisture diffusivity was calculated by using the simplified Fick's second law of diffusion model (Doymaz, 2004) as given in Eq (5).

$$\frac{\partial M}{\partial t} = D_{eff}.\nabla^2 M \qquad \ldots(5)$$

Where,

M = moisture content (kg water/kg dry matter);

t = time (s);

D_{eff} = effective moisture diffusivity, (m^2/s);

∇^2 = differential operator.

The solution of Fick's second law in sphere geometry, with the assumption that moisture migration was caused by diffusion, negligible shrinkage, constant diffusion coefficient, and temperature, was given by Crank (1975) as follows:

$$MR = \frac{8}{\pi^2}\sum_{i=1}^{n}\frac{1}{(2n-1)^2}exp\left(\frac{-(2n-1)^2\pi^2 D_{eff^t}}{4H^2}\right) \quad \ldots(6)$$

Where,

H = is the half thickness of the slab m;

n = 1, 2, 3 … the number of terms taken into consideration.

For long drying time Eq (7) can be simplified further (Lopez *et al.* 2000; Doymaz, 2004) as:

$$ln(MR) = ln\frac{8}{\pi^2} - \frac{\pi^2 D_{eff^t}}{4L^2} \quad \ldots(7)$$

The diffusivities are typically determined by plotting the experimental drying data in terms of *ln* (MR) vs drying time (t) in equation (8), because the plot gives a straight line with the slope as follows:

$$Slope = \frac{\pi^2 D_{eff}}{4L^2} \quad \ldots(8)$$

Where,

L = half thickness

1.4 Evaluation of Quality parameters for the grape raisins:

1.4.1 Total soluble solids

The TSS was determined by using a hand refractometer (M/s. Atago, Japan) and the values were corrected at 20 °C with the help of a temperature correction table (Mazumdar and Majumder, 2003). For the fresh berries, the grapes were squeezed and the juice extracted. The fresh juice was placed on a prism plate to record the visible value on the scale. The reading of the juice sample as °Brix was obtained, and the digital reading of the Total soluble solids was expressed accordingly. Three observations were taken for replication.

For the raisins, 5 g of raisins sample was crushed and mixed with 15 ml of distilled water (A.O.A.C, 1990). Then the juice prepared was used for the TSS determination. The TSS of the juice was determined as per the procedure explained earlier. Three observations were taken and used as replications.

1.4.2 Titratable acidity

The acidity of fresh berries and raisins were estimated by adopting the procedure given by Ranganna (1978). The fresh berries of grapes was crushed, and juice was extracted. 10 ml of juice was extracted and diluted to the volume of 100 ml with distilled water. Using the phenolphthalein indicator, 10 ml of diluted juice was titrated against 0.1N NaOH till it changed the juice to the pink colour of the endpoint.

Titrable acidity of raisins was determined as per the procedure (A.O.A.C., 1975). 10 g of sample was grounded and added with a small quantity of distilled water. The content was filtered using filter paper. 10 ml of filtrate was used for titration to estimate the acidity, as was done for fresh juice. The titrated acidity was expressed in percentage.

$$\text{Titratable acidity (\%)} = \frac{N \times T \times E}{W \times V \times 1000} \times 100 \quad \ldots(9)$$

Where,

N = Normality of alkali

T = Titrate reading, ml

E = Equivalent mass of acid, g

W = Weight of the sample, g

V = Total volume of the sample, g

1.4.3 pH

pH of fresh grapes and dried grapes (raisins) for Treatment T_1 and Treatment T_2 was measured using a digital pH meter. The digital pH meter is first calibrated by using 4 pH and 7 pH buffer solution. The electrode was washed with distilled water and blot led with tissue paper. 10 ml of fresh grape juice was taken in a beaker, then the tip of the electrode and temperature probe were submerged into the sample. The pH reading is displayed on the primary LCD, and the temperature on the secondary one.

The pH of fresh grape juice was determined by three replications.

Grape raisins were dissolved in distilled water 1:2.5 (sample: water) and kept for 4 hours (Babaji, 2009). Thereafter, after the solution was stirred well the pH of the solution was determined as per the procedure explained earlier.

1.4.4 Reducing sugars

The reducing sugars of berries were determined as per the procedure of Ranganna (1978). 10 ml of fresh grape juice was squeezed was ground well into juice with a small quantity of water. Then, the sample juice volume was made up to 100 ml with distilled water using a volumetric flask. And for raisins, 10 g of sample was ground well into juice with 20 ml of water then the sample juice volume was made up to 100 ml with distilled water using a volumetric flask. This solution was neutralized with 20 % NaOH using a few drops of phenolphthalein indicator until the solution turned pink and acidified with 1 N HCl until it caused the pink color to disappear. To this 2 ml of 45 % lead acetate was added, shaken well, and kept to settle for 10 minutes. Then 2 ml of 22 % potassium oxalate was added to remove excess lead, and the volume was made up to 250 ml with distilled water. The content was filtered using filter paper. Reducing sugars in the lead-free extract was then estimated by taking the solution into a burette and titrated against mixed Fehling's solutions (A and B).

10 ml of mixed Fehling's solution was taken into a 250 ml conical flask to which 50 ml of water was added and ran the burette was put into the flask to the required volume of sugar solution as was prejudged incrementally to reduce the Fehling's solution which indicated by turning the solution to brick red color on boiling. Then, the boiling was continued for 2 minutes, and added methylene blue indicator was titrated with sugar solution on heating until the indicator was completely decolorized and formed a brick red color precipitate, which was the endpoint. The titrate value was obtained and calculated as below (Eq. 10). The experiment was repeated three times to get the replication.

$$Reducing\ sugar\ \% = \frac{100}{burettereading} \times \frac{volume\ prepared}{inital\ volume} \times GV\ of\ fehling'ssolution \quad \ldots(10)$$

GV = Glucose value

1.4.5 Total sugars

Total sugars of fresh berries and raisins were for Treatment T_1 and Treatment T_2 estimated by adopting the Lane and Eynon method (Ranganna, 1978). Exactly 50 ml of lead-free filtrate was taken to 100 ml volumetric flask. To it 10 ml of HCl (5 ml Conc HCl + 5 ml water) was added and allowed to remain stand for 24 hours at ambient temperature in dark room. The inverted solution was neutralized, and the volume was made up to 100 ml with distilled water. This solution was taken into burette and titrated against mixed Fehling's solutions as was done for reducing sugars. The aliquot was determined as inverted sugars, and the total sugar content was calculated below (Eq.11). The experiment was repeated three times to get the replication.

Total sugar (%) =

$$\frac{Factor \times Dilution}{Titrereading \times Weightn\ of\ sample} \times 100 \quad \ldots(11)$$

1.4.6 Non-Reducing Sugars

The non-reducing sugars present in the samples were derived by deducting the reducing sugars from total sugars.

% Non-reducing sugars = [% of Total sugars – % of Reducing sugars]

1.4.7 Ascorbic acid (Vit. C)

The ascorbic acid (vit. c) was determined for fresh grape juice samples and grapes raisins for Treatment T_1 and Treatment T_2, respectively. Determination of ascorbic acid was done by 2, 6-dichlorophenol indophenol dye method of Johnson (1948) as described by Ranganna (1986). 3% metaphosphoric acid (HPO_3) is prepared by dissolving sticks of HPO_3 in distilled water, Dye solution was made up by adding 2,6 dichlorophenol metaphosphoric acid solution, and the volume was made to 100 ml using a volumetric flask. The extract was filtered by using filter paper.10ml aliquot was taken by using a pipette into the conical flask and titrated against standard dye solution at room temperature. End point of the titration was the pink colour. The ascorbic acid content of the fresh grapes was calculated taking into consideration the dye factor as given below.

For grape raisins, 10 g raisins were taken from each replication was grounded well using a small amount of 3% meta-phosphoric acid (HPO_3), and the volume was made up to 100 ml with 3% meta-phosphoric acid using a volumetric flask. The ascorbic acid determination procedure was performed as per the procedure discussed earlier.

Ascorbic acid (mg/100g) =

$$\frac{\text{Titre value} \times \text{Dye Factorx} \; \text{Volume made up}}{\text{Aliquate of extract taken for estimation} \times \text{Weightn of sample}} \times 100 \qquad \ldots(12)$$

1.4.8 Colour

The fresh grapes and dried grapes was used to measure the colour value (L,a, and b) by using a colorimeter (Konica minotta, Japan model-Meter CR-400). The equipment was calibrated against standard white tile and black tile. Around 20 g of fresh grape and dried grapes (grape raisins) was taken in the glass petri dish, the equipment was placed on the sample petri dish. The color was recorded in terms of L= lightness (100) to darkness (0); *a* = Redness (+60) to Greenness (-60); *b* = yellowness (+60) to blueness (-60). The yellowness index of the fresh grapes and grapes raisins was determined from L, a, and b values as per equation (13) reported by (Rhim *et al.* 1999);

$$YI = \frac{142.86b}{L} \qquad \ldots(13)$$

Where,

L = Lightness to darkness

B = Yellowness to blueness

1.4.9 Hardness

The texture of fresh grape and dried grape raisins was measured with TexVol instruments TVT-300 XP texture analyzer. A fresh grape and dried grape sample were placed on a hollow planar base to compression test with a spherical probe and size 5 mm diameter and pre-test speed was 0.5 mm/s, compression depth was 4.5 mm, and trigger force was 5 g for fresh grapes and dried grapes. The maximum compression force of a rupture test of each sample was used to describe the sample texture in terms of hardness. All tests were triplicated, and the average values were reported.

1.5 Sensory analysis

The sensory attribute of dried grapes (raisins) of Treatment 1 and Treatment 2 was determined with trained panelists as per a point hedonic scale. The Panelists were trained for the product testing and were familiar with product sensory evaluation. The dried grapes (raisins) samples were placed into petri dish dried grapes (raisins) were coded as A and B for evaluation of sensory parameters i.e. color, flavor, texture, and taste attributes. Code A and B for Treatments T_1 and T_2, and code C was for the control sample. The rating was based on nine-point hedonic scales. 09 scales for colour, 09 scales for flavor attribute, 09 scales for texture attribute, and 09 scales for taste. The attributes were summed up for a total score 36 for each panelist for each treatment. The average score for a total 14 panelists has been reported. The data were analyzed statistically for the significance of each attribute by ANOVA.

2. RESULTS AND DISCUSSION

Fig. 2 shows moisture content (db) % with respect to time (min) of grapes treated with T_1 (2.5% NaOH plus 2% KMS) and T_2 (2.5% potassium carbonate + 2% ethyle oleate) dried by open-air sun drying. The grapes were dried from an average initial moisture content of 370.57% (db) to 14.39% (db) for Treatment 1 and 370.57% (db) to 14.18% (db) for Treatment 2. It took around 85 hrs (11 days) and 60 hrs (8 days) to dry the product pre-treated with Treatment 1 and Treatment 2, respectively.

Fig. 3 shows the drying rate (g water removed/100 g of bone dry material; /min) with respect to moisture content % (db) of grapes dried by open-air sun drying. The drying took place in a falling rate period for both treatments. Similar behavior had been observed in the literature for grapes pre-treated with alkali solution and dried in a domestic microwave oven and open-air sun drying (Kostaropoulos *et al.* 1995). The initial drying rate of treated grapes decreases from 0.1243 g to 7.30 × 10^{-3} g water removed /100 gm of dry solid /min) and 0.0766 g to 1.01 × 10^{-2} g water removed /100 gm of dry solid/min) for Treatment T_1 and Treatment T_2 respectively.

Fig.4 shows the variation in moisture ratio with respect to time in minute. During the drying

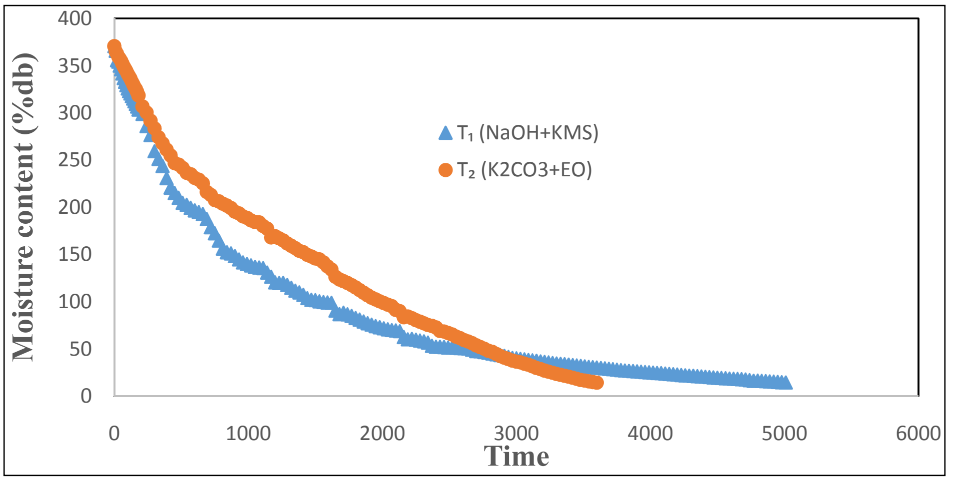

Fig. 2: Moisture content % (db) versus time (min) sun drying for grape

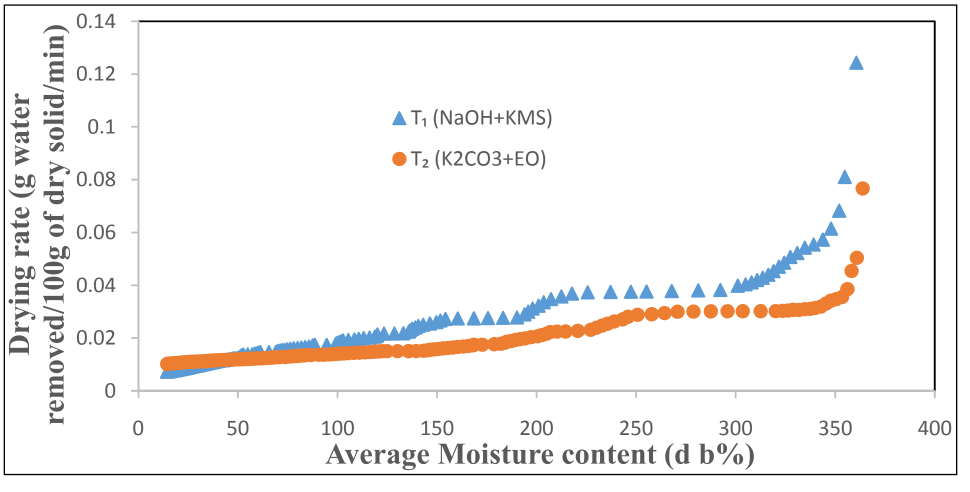

Fig. 3: Drying rate (g water removed/100 g of bone dry material/min) versus moisture content % (db) of grape dried by sun drying

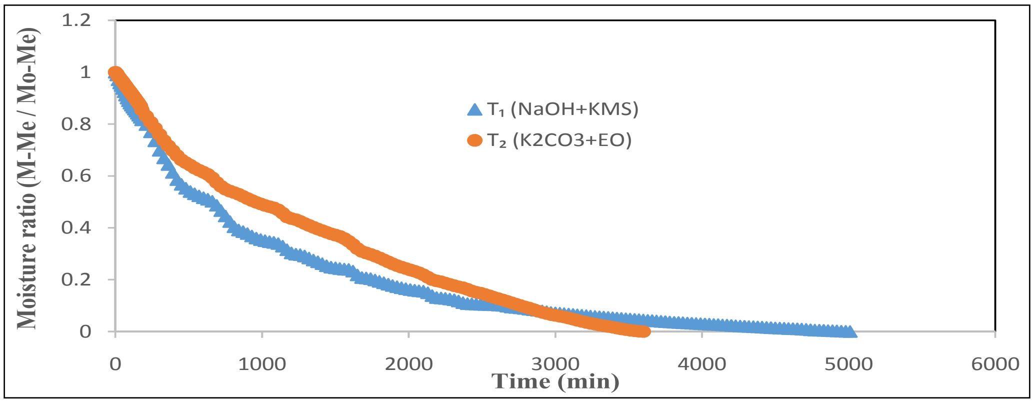

Fig. 4: Variation in moisture ratio with respect to time, min for grape during sun drying

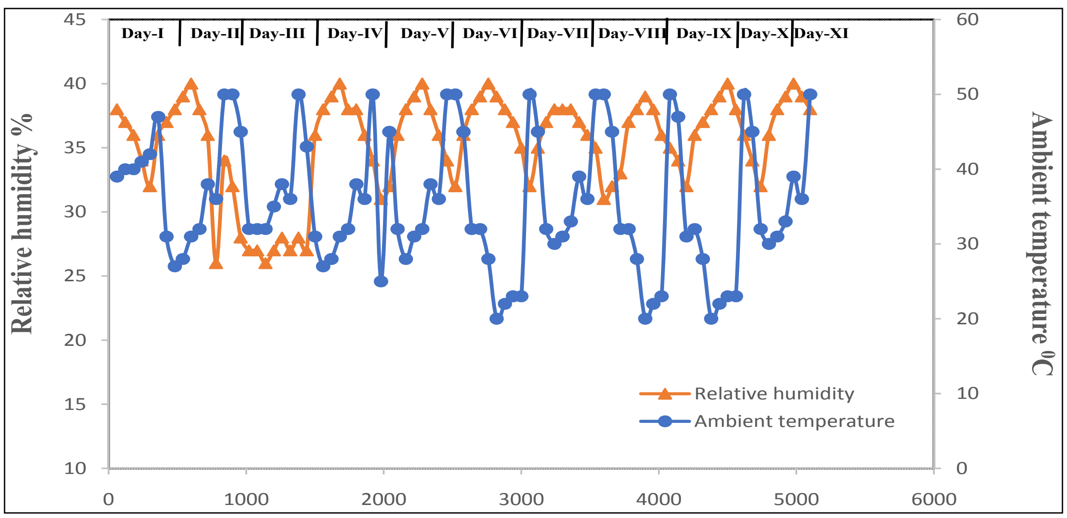

Fig. 5: Variation in ambient temperature and relative humidity with time in open air sun drying of grapes

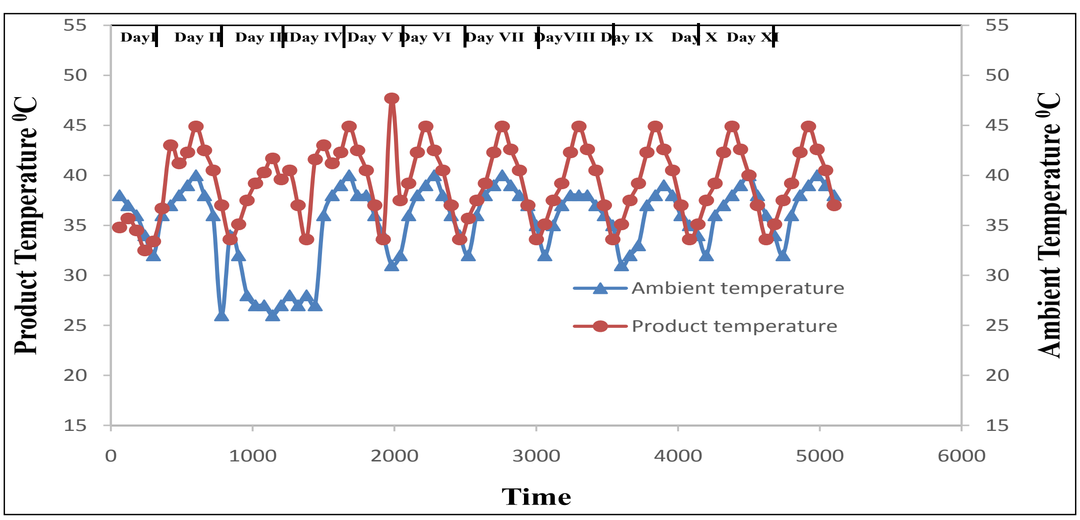

Fig. 6: Variation in product temperature and ambient air temperature with time

experiment moisture ratio decreases from 1 to 1.73×10^{-6} and 1 to 1.95×10^{-7} for the pre-treatment solution Treatment 1 and Treatment 2, respectively. Similar curve was observed for sultana grapes with alkali solution and domestic microwave oven and open-air sun drying (Kostaropoulos *et al.* 1995).

Fig. 5 shows the change in the ambient temperature (°C) and relative humidity (%) with respect to the time during the 11 days of open-air sun drying. Relative humidity ranges from 20 to 50 %, the ambient air temperature is 26 to 40°C, and the average ambient temperature is 35.42 °C.

Fig. 6 shows the variation in product temperature and ambient air temperature variations with respect to time during 11 days of drying of grapes. The average product temperature was 39.23°C. The average ambient temperature was 35.42 °C. The ambient air temperature was in the range 27 -40 °C. The product temperature ranges from 32.5 to 44.9 °C.

2.1 Evaluation of thin layer-drying model of grapes treated with T_1 solution and dried by Open air sun drying

Tables 2 and 3 show the model parameters of various models fitted to the experimental data for open-air sun drying of grapes for the Newton model, Page model, Henderson and Pabis model, Exponential, Exponential two-term model, Approximation of diffusion, Logarithmic model, Modified page equation II etc.

Among the models fitted to the experimental data to Treatment-1 and Treatment-2, the Exponential two term drying model was well fitted to the experimental data with r^2 = 0.9991, MSE = 8.481×10^{-5}, chi-square (χ^2) = 0.0150 for Treatment-1 and the Logarithmic drying model was well fitted to the experimental data with r^2 = 0.9947, MSE = 4.996×10^{-5}, χ^2) = 0.0649 for Treatment-2.

Table (2 and 3) show the statistical regression results of the different models, including the drying model coefficients and comparison criteria used to evaluate the goodness of the fit, including the r^2, χ^2 and RMSE of grape at open sun drying. Non-linear regression analysis was done according to the nine thin layer models for moisture ratio data. In

Table 2: Model parameters, R^2, RMSE and Chi square (χ^2) values of grape pre- treated with Treatment (T_1) and dried by the open air sun drying

Sl. No.	Model name	Model Parameters	R^2	MSE	χ^2
1	Newton	$k = 9.859 \times 10^{-4}$	0.9964	5.557×10^{-4}	0.0994
2	Page	$k = 2.461 \times 10^{-3}$ $n = 0.8717$	0.9986	1.187×10^{-4}	0.0211
3	Modified Page	$k = 1.017 \times 10^{-3}$ $n = 0.8717$	0.9986	1.187×10^{-4}	0.0211
4	Henderson and Pabis	$a = 0.9541$ $k = 9.338 \times 10^{-4}$	0.9959	3.557×10^{-4}	0.0633
5	Exponential	$k = 9.859 \times 10^{-4}$	0.9964	5.557×10^{-4}	0.0994
6	Exponential two term	$a = 0.2494$ $k = 3.094 \times 10^{-3}$	0.9991	8.481×10^{-5}	0.0150
7	Logarithmic	$a = 0.9468$ $k = 9.933 \times 10^{-4}$ $c = 1.656 \times 10^{-2}$	0.9964	2.944×10^{-4}	0.0521
8	Modified Page equation-II	$k = 0.8116$ $L = 27.8182$ $n = 0.8717$	0.9986	1.187×10-4	0.0211

Table 3: Evaluation of thin layer-drying model of grape pre-treated with Treatment-(T_2) and dried by open air sun drying

Sl. No.	Model name	Model Parameters	R^2	MSE	χ^2
1	Newton	$k = 7.574 \times 10^{-4}$	0.9888	1.096×10^{-3}	0.1446
2	Page	$K = 6.550 \times 10^{-4}$ $n = 1.0197$	0.9889	1.0936×10^{-3}	0.1432
3	Modified Page	$k = 7.551 \times 10^{-4}$ $n = 1.0197$	0.9889	1.093×10^{-3}	0.1432
4	Henderson and Pabis	$a = 0.9909$ $k = 7.499 \times 10^{-4}$	0.9892	1.0914×10^{-3}	0.1429
5	Exponential	$k = 7.574 \times 10^{-4}$	0.9888	1.096×10^{-3}	0.1446
6	Exponential two term	$a = 0.0110$ $k = 0.0674$	0.9893	1.089×10^{-3}	0.1427
7	Logarithmic	$a = 1.1019$ $k = 5.504 \times 10^{-4}$ $c = -0.1407$	0.9947	4.996×10^{-3}	0.0649
8	Modified Page equation-II	$K = 0.7013$ $L = 30.5810$ $n = 1.0197$	0.9889	1.093×10^{-3}	0.1432

open sun drying and pre-treated with Treatment-1and Treatment-2 case r^2 values for the model were equal to 0.999 and 0.994 indicating a good fit. The model parameters like a and k are the characteristics constant, k is diffusivity (diffusion coefficient, and it is temperature dependent). The model parameter i.e., $a = 0.2494$, $k = 3.094 \times 10^{-3}$ for Treatment-1 and $a = 1.1019$, $k = 5.540 \times 10^{-4}$, $c = -0.1407$ for Treatment-2. Doymaz (2012) found the Midilli *et al.* model well fitted to the open sun drying of grape.

2.2 Effective moisture diffusivity of grapes dried by open air sun drying

Fig. 7 shows Ln (MR) versus time (minute) for open-air sun drying of grapes and pre-treated with Teatment-1and Treatment-2. The graph shows the straight line curve. The straight line equation $y = mx + c$ where the m is the slope of line. Effective diffusivity (*Deff*) at time for treated grape which was calculated by equation (5). Effective Diffusivity (*Deff*) at time (*t*) for treated Grape drying by open air sun for Teatment-T_1 and Treatment-T_2 was 5.07×10^{-9} m²/s and 6.08×10^{-9} m²/s respectively. Generally, effective diffusivity is used to explain the mechanism of moisture movement during drying and the complexity of the process (Kashaninejad *et al.* 2007; Falade and Solademi, 2010). Doymaz (2012) observed results for grapes treated with 2.5% potassium carbonate plus 0.5% olive oil and open sun drying was 1.66×10^{-11} m²/s also, these values lie within the general range of 10^{-12} to 10^{-8} m²/s for the food material.

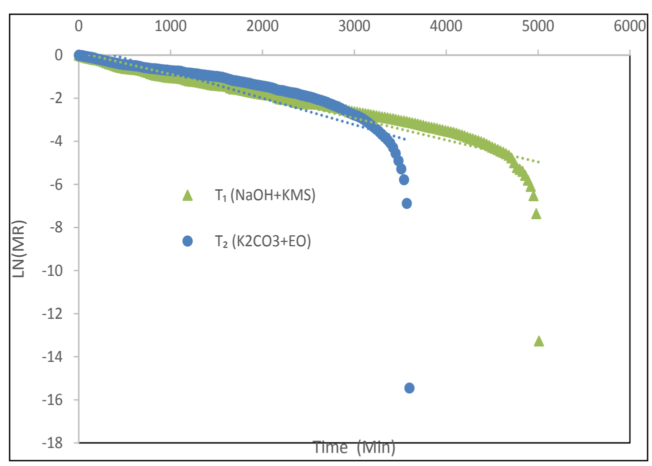

Fig. 7: LN (MR) versus Time (Minutes) for pre-treated grapes for Treatment T_1 and Treatment T_2 dried with open sun drying

2.3 Nutritional quality of treated grapes dried by open air sun drying

Table 4 shows the various quality parameters (a) moisture, (b) TSS, (c) titratable acidity, (d)pH, (e) reducing sugar, (f) total sugar, (g) non-reducing sugar, (h) Ascorbic acid (i) color (yellowness index) (j) hardness of grapes before drying and after drying by open sun drying and pre-treated with Treatment-1and Treatment-2 solution.

2.3.1 Moisture content

Table 4 (a) shows the moisture content of grapes before drying and after drying. The moisture content of grapes before drying was 405.27% (db), and the moisture content ranged after drying from 12.34 to 18.93 % (db) in both pre-treatment and open-air sun drying. The average moisture content was 14.55±3.80 % (db) in Treatment-1solution and 14.40±2.60 % (db) in Treatment-2 solution. Irrespective of pre-treatment methods and conditions of the drying, the moisture content of grapes decreased after drying. Lowest changes in moisture content was observed in the Treatment-1 and Treatment-2 solution of grapes, followed by open-air sun drying. The decrease in moisture content of grapes after open sun drying was significant at $p \leq 0.05$.

Adsule and Banerjee (2003), Winkler *et al*. (1962), Gowda *et al.* (1997) reported the desirable moisture content for grape raisins are 15.00 to 16.50%; 10 to 15 % and 14.1 to 14.9% respectively.

2.3.2 Total soluble solids

Table 4 (b) shows the total soluble solids of grapes before drying and after drying. The total soluble solids of grapes before drying was 19.9°B±0.492°B and the TSS increased after drying from 71 to 73 °B in both pre-treatments. The average TSS was 72.67^{O}B in Treatment-1 and 72°B in Treatment-2. Irrespective pre-treatment solution and conditions of the drying, TSS of grapes increases after drying. The increases in total soluble solids of grapes after open sun drying might be attributed due to concentration of fruit flavors and mass/solids during drying. TSS was increased more in Treatment-1 solution. This increase of total soluble solids was significant at $p \leq 0.05$.

Mane *et al*. (2003) reported that TSS of grape raisins was 79.8 for Manikchaman variety.

2.3.3 Titratable acidity

Table 4 (c) shows the titratable acidity of grapes before drying and after drying. The titratable acidity of grapes before drying was 0.67% ± 0.17, and the titratable acidity increased after drying from 2.37 to 2.82 % in both pre-treatments. The titratable acidity was 2.75 % for Treatment-1 and 2.43% for Treatment-2 solution. Irrespective of pre- treatment methods and conditions of the drying, the titratable acidity of grapes increases after drying. The lowest changes of titratable acidity were observed in Treatment-2 as compared to Treatment-1. The increases in titratable acidity of grapes after open sun drying was significant at $p \leq 0.05$.

Gowda *et al.* (1997); Dan *et al.* (1977) reported that the acidity of grape raisins was in the range from 1.92 to 2.53% and 1.22 to 2.27%, respectively.

2.3.4 pH

Table 4 (d) shows the pH of grapes before drying and after drying. The pH of grapes before drying was 4.3 ± 0.173, and observed that pH was increased after drying. It was 4.30 to 4.80 in both pre-treatments. The average pH was 4.77 ± 0.06 in Treatment-1 and 4.37±0.06 in Treatment-2 solution. The increases in pH of grapes after drying might be attributed to the effect of air on solid content. Lowest changes of pH were observed in both pre-treatment solutions of grapes followed by open sun drying.

Doneche (1990) observed that pH range 2.8 to 6 of raisins prepared by different pre-tretments from Thompson seedless cultivar. Tupe (2007) observed that pH of raisins prepared by different pre-treatments ranged from 2.00 to 4.65 in Thompson seedless.

2.3.5 Reducing sugar

Table 4 (e) shows the reduced sugar of grapes before drying and after drying. The reducing sugar of grapes before drying was 17.395 ± 0.716 % and the reduced sugar increased after drying from 62.50 to 63.50 % in both pre-treatment. The reducing sugar was 63.10±0.53 % in Treatment-1and 62.76±0.46 in Treatment-2 solution. Irrespective of pre-treatment methods and conditions of the drying, reducing the sugar of grapes increases after drying. Lowest changes of reducing sugar were observed in Treatment-2 solution of grapes followed by open sun drying.

The increases in reduced sugar of grapes after open sun drying might be attributed due to the concentration of fruit flavours and mass/solids during drying. This increase in reducing sugar was significant at $p \leq 0.05$. Gowada *et al.* 1997; Beslic *et al.* 2009 reported that reducing sugar in raisins was 68% and 68.2%, respectively.

2.3.6 Total sugar

Table 4 (f) shows the total sugar of grapes before drying and after drying. The total sugar of grapes before drying was 19.417± 0.087% and the total sugar increased after drying from 64.10 to 65.78 % in both pre-treatment. The total sugar was 65.67± 0.10 % in Treatment-1 and 65.22± 0.97 in Treatment-2 solution. Irrespective of pre-treatment methods and conditions of the drying, the total sugar of grapes increases after drying. Lowest changes of total sugar were observed in Treatment-2 as compared to Treatment-1 of grapes followed by open sun drying. The increases in total sugar of grapes after open-air sun drying might be attributed due to the concentration of fruit flavors and mass/solids during drying. This increase in total sugar was significant at $p \leq 0.05$. Dan *et al.* 1977 prepared raisins from different varieties and reported that the total sugar content ranged from 58.09 to 62.00 percent. Gowada *et al.* 1997 reported that the total sugar in raisins was 68.6% for Thompson seedless variety grape raisins.

2.3.7 Non-reducing sugar

Table 4 (g) shows the non-reducing sugar of grapes before drying and after drying. The non-reducing sugar of grapes before drying was 2.015 ± 0.751% and observed that non-reducing sugar had no more changes after drying. It was 1.60 to 3.41 % in both pre- treatment. The non-reducing sugar was 2.67 ± 0.44 % in Treatment-1and 2.46 ±0.84 in Treatment-2 solution. The lowest changes of non-reducing sugar were observed in pre- treatment solution of grapes followed by open-air drying.

Mane *et al.* 2003; Beslic *et al.* 2009 reported non-reducing sugars from 3.50 to 4.80 and 3.5 to 4.8 per cent in grape raisins.

2.3.8 Ascorbic acid

Table 4 (h) shows the ascorbic acid of grapes before drying and after drying. The ascorbic acid of grapes before drying was 5.88 ± 0.740%, and the ascorbic acid increased after drying from 20.00 to 20.85 mg in both pre-treatments. The ascorbic acid was 20.98 ± 0.29 mgin Treatment-1 and 20.73 ± 0.13 mg in Treatment-2 solution. Irrespective of pre-treatment methods and the condition of the drying, ascorbic acid of grapes increases after drying. Lowest changes of ascorbic acid were observed in Treatment-2 solution as compared to Treatment-1 solution of grapes followed by open-air sun drying. The increases in ascorbic acid of grapes after open sun drying might be attributed due to the concentration of fruit flavors and mass/solids during drying. This increase of ascorbic acid was significant at $p \leq 0.05$.

Chavan *et al.* 1992; Kulkarni *et al.* (1986) reported ascorbic acid 21.1 to 31.3 and 7.6 to 15.5 mg per 100 g of raisins prepared by various methods.

2.3.9 Colour

Table 4 (i) shows the yellowness index of grapes before drying and after drying. The Yellowness index of grapes before drying was 81.35 ± 0.99 and the yellowness index decreased after drying from 63.07 to 76.02 in both pre-treatments. The yellowness was 71.72± 3.84 in Treatment-1 and 65.17 ± 1.48 in

Treatment-2. Irrespective of pre-treatment methods and conditions of the drying, the yellowness index of grapes decreases after drying. Lowest changes of yellowness index was observed in Treatment-1of grapes followed by open-air sun drying compared with Treatment T_2.

The decrease in the yellowness index of grapes after convective hot air drying might be attributed to temperature effect. These changes in Yellowness were significant at $p \leq 0.05$.

Doymaz (2002) reported that colour L, a, and b values of grapes raisins were in the range of 17.37-22.31, 3.84-4.55, and 4.28-5.27, respectively and the yellowness index was 35.20 to 33.74.

Matteo *et al.* (2000) reported that the colour L, a, and b value of grapes raisins was 41.8 ± 6.8. 2.5 ± 0.2 and 13.8 ± 0.9, respectively and the yellowness index was 47.16.

2.3.10 Hardness

Table 4 (j) shows the hardness of grapes before and after drying. The hardness of grapes before drying was 0.62 ± 0.14 and after drying it changes from 2.33 to 4.58 N in both pre-treatment. The hardness was 3.76 ± 1N in Treatment-1 and 2.55 ± 0.31 N in Treatment-2 solution. Xiao *et al.* 2010 reported that the hardness of grape raisins was 9.53 ± 0.6 N when dried at 50°C.

Based on the nutritional analysis and the hardness and Yellowness index the raisins of treatment T_1 has more TSS, Titrable acidity, Reducing sugar, total sugar and ascorbic acid and better hardness and yellowness index.

2.4 Best treatment from Treatment (T_1) and Treatment (T_2)

The desirable qualities of grape raisins should have more TSS, more Titrable acidity, more Reducing sugar, more total sugar, more ascorbic acid, more yellowness index and more hardness.

Treatment T_1 Treatment T_2

Fig. 8: Photograph of the raisins prepared from Treatment T_1 and Treatment T_2

3.4.1 Colour

Table 5(a) shows sensory score for colour ranged from 6.75 to 7.12, the higher score 7.12 for control Treatment. The colour of control Treatment highly accepted by the sensory panelist. The sensory values for colour were non-significant at $p \leq 0.05$.

Table 4: Quality parameter of grapes before and after drying

Quality parameter	Before drying	Treatment T_1 = 2.5% NaOH for 2-3 sec + 2% KMS + open sun drying	Treatment T_2 = 2.5% potassium carbonate + 2% ethyleoleate + open sun drying	S.Em (±)	C.D at 5 %
(a) Moisture content (%)	405.27 ± 0.745	14.54 ± 3.80	14.40 ± 2.62	1.541	5.332
(b) Total soluble solids (°B)	19.90 ± 0.492	72.67 ± 0.58	72±1.00	0.384	1.331
(c) Titratable acidity (%)	0.678 ± 0.020	2.75 ± 0.06	2.43 ± 0.06	0.031	0.106
(d) pH	4.30 ± 0.173	4.77 ± 0.12	4.37 ± 0.06	0.027	0.094
(e) Reducing sugar (%)	17.395 ± 0.716	63.10 ± 0.53	62.76 ± 0.46	0.232	0.804
(f) Total sugar (%)	19.417 ± 0.087	65.67 ± 0.10	65.22 ± 0.97	0.325	1.125
(g) Non- reducing sugar	2.015 ± 0.751	2.67 ± 0.64	2.46±0.84	0.352	1.219
(h) Ascorbic acid (mg)	5.88 ± 0.740	20.98 ± 0.29	20.73±0.13	0.105	0.363
(i) Colour (yellowness index)	81.35 ± 0.99	71.72 ± 3.84	65.17± 1.48	1.374	4.753
(j) Hardness (N)	0.66 ± 0.14	3.76 ± 1.00	2.55± 0.31	0.350	1.212

Treatment T_1

Treatment T_2

Fig. 8: **P**hotograph of the raisins prepared from Treatment T_1 and Treatment T_2

Table 5: Sensory score of grapes pretreated with Treatment T1 and T2 and dried by open sun drying

Parameter	Control	Treatment 1	Treatment 2	SEm(±)	CD 5% @ p≤0.05
Colour (a)	7.12	6.75	6.95	3.21	9.20
Flavour (b)	7.10	7.30	7.29	2.65	7.60
Texture (c)	7.20	7.37	7.22	2.77	7.95
Taste (d)	7.24	7.25	7.08	2.52	7.22
Overall acceptability (e)	7.30	7.34	7.30	2.92	8.36

2.4.2 Flavour

Table 5 (b) shows sensory score for flavour ranged from 7.10 to 7.30, the higher score 7.30 for Treatment-1. The flavour of Treatment-1 highly accepted by the sensory panelist. The sensory values for flavour were non-significant at p≤0.05.

2.4.3 Texture

Table 5 (b) shows sensory score for texture ranged from 7.20 to 7.37, the higher score 7.37 for Treatment-1. The texture of Treatment-1 is highly accepted by the sensory panelist. The sensory values for texture were non-significant at p≤0.05.

3.4.4 Taste

Table 5 (b) shows sensory score for tasteranged from 7.08 to 7.25, the higher score 7.25 for Treatment-1. The taste of Treatment-1 highly accepted by the sensory panelist. The sensory values fortastewere non-significant at p≤0.05.

2.4.5 Overall acceptability

Table 5 (b) shows sensory score for Overall acceptability ranged from 7.30 to 7.34, the higher score 7.34 for Treatment-1. The Overall acceptability of Treatment-1 highly accepted by the sensory panelist. The sensory values for Overall acceptability were non- significant at p≤0.05.

From the data of quality analysis of dried grapes (i.e. acidity, pH, TSS, reducing sugars, total sugars, non-reducing sugar, ascorbic acid, hardness, color (yellowness index), drying time) for Treatment T_1 and Treatment T_2 showed that Treatment T_1 had highest retention of a quality parameter as compare to Treatments T_2. The best sensory score of the product have been obtained from sensory analysis,

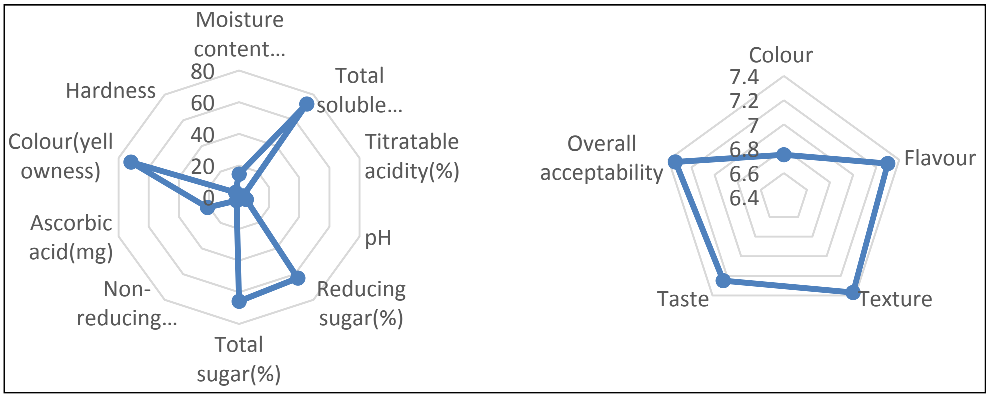

Fig. 9: (a) Quality analysis and **(b)** sensory analysis of grapes pretreated with Treatment T_1 and dried by open sun drying

which was grapes pretreated with Treatment T_1 and dried by open-air sun drying had achieved the highest color 6.75, flavor 7.30, texture 7.37 and taste 7.25. From both quality properties, colour measurement and sensory analysis the best product i.e. grapes pretreated with Treatment T_1 and dried by open sun drying satisfactorily retains parameters with desirable quality.

CONCLUSION

1. The grapes were dried from average initial moisture content of 370.57% (db) to 14.39% (db) for Treatment-1 and 370.57% (db) to 14.18% (db) for Treatment-2. It took around 85 and 60 hrs to dry the product with pre-treated with Treatment 1 and Treatment 2.
2. Among the models fitted to the experimental data to Treatment-1 and Treatment-2, the Exponential two term drying model was well fitted to the experimental data with $r^2 = 0.9991$, MSE = 8.481×10^{-5}, chi square (χ^2) = 0.0150 for Treatment-1 and the Logarithmic drying model was well fitted to the experimental data with $r^2 = 0.9947$, MSE = 4.996×10^{-5}, chi square (χ^2) = 0.0649 for Treatment-2.
3. Effective Diffusivity (D_{eff}) at time (t) for treated Grape dried by open sun drying for Teatment-T1and Treatment-T2 was 5.07×10^{-9} m²/s. and 6.08×10^{-9} m²/s respectively.
4. Grapes pretreated with Treatment T1 and dried by open sun drying satisfactorily retains parameter with desirable quality parameter moisture content of raisins was 14.54%, TSS 72.67°B, Titrable acidity 2.75%, pH 4.77, Reducing sugar 63.10%, Total sugar 65.67 %, Non-reducing sugar 2.67, Ascorbic acid 20.98 mg, yellowness 71.72 and hardness 3.76 for Treatment-1.

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