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Assessment of postharvest dehydration kinetics and skin mechanical properties of "Muscat of Alexandria" grapes by response surface methodology

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ABSTRACT

The dipping of berries in a dilute solution of sodium hydroxide during a short time was evaluated as pretreatment undertaken prior to convective dehydration of winegrapes. The impact of the sodium hydroxide content and dipping time on weight loss (WL) at different dehydration times was thoroughly assessed using central composite design (CCD) and response surface methodology (RSM). Furthermore, the effects of these two variables were also investigated on the skin mechanical properties of dehydrated grapes. The effect of these two pretreatment factors on the dehydration kinetics and skin hardness was satisfactorily fitted to regression models. The berry pretreatment with low sodium hydroxide contents (from 10 to 20 g/L) facilitated the dehydration process during the first five days when dipping times longer than 300 s were used. From the seventh day of dehydration, at which time the average WL% was close to 50, the highest values of WL% were obtained using intermediate sodium hydroxide contents and dipping times (around 45 g/L and 185 s, respectively). Because skin hardness affects the dehydration kinetics during postharvest withering, the strongest decrease in skin hardness corresponded to these last berry pretreatment conditions, whereas the greatest increase required the highest sodium hydroxide contents and longest dipping times. The quality of berries dehydrated may be influenced by the pretreatment conditions used, and the present study contributes to increase the knowledge on this effect to a better management of the alkaline pretreatment and dehydration process.

Keywords: grape dehydration kinetics, alkaline pretreatment, berry skin mechanical properties, response surface methodology, Muscat of Alexandria grapes

1. Introduction

Dehydration is a process traditionally used to preserve food despite major structural and organoleptic changes occur. Particularly in fruits, the characteristics of the final product are strongly dependent on the type of drying, the effect of processing variables and structural properties of the fresh material (Delgado and Barbosa de Lima 2015). In fact, the grape cultivar and drying method influence the sensory characteristics and consumer preference of raisins (Angulo et al. 2007). Also some renowned wines, such as Passito wines, Sauternes, Tokaj, Porto, Pedro Ximénez, or Amarone as well as many others less known, fall into the category of special wines that are locally produced, in viticultural areas around the world, from dehydrated grapes (Mencarelli and Tonutti 2013).

In many Mediterranean regions where a great water loss is required, as for raisins as for wine, grapes are naturally dehydrated by sun exposure when the climatic conditions are favorable (Serratosa et al. 2008; López de Lerma et al. 2014). In contrast, in Italy, the most commonly used dehydration method for winegrapes is natural postharvest withering indoors in ventilated rooms under uncontrolled environmental conditions (Giacosa et al. 2012). When not regulated by specific rules imposed by a product specification, the postharvest withering process can be facilitated in terms of speed and safety by forced-air convection in chambers under controlled thermohygrometric conditions (Giacosa et al. 2012; Serratosa et al. 2014; Delgado and Barbosa de Lima 2015).

The composition and structure of fruit surface tissues determine the water potential gradient during dehydration. A recent study has shown the important role of the fruit cuticle in postharvest water loss (Lara et al. 2014). Nevertheless, cuticular permeability to water is strongly influenced by the fruit maturity, environmental conditions and genetic factors (Lara et al. 2014). Various chemical pretreatments are widely used to increase the dehydration rate through microstructural changes in the epicuticular wax layer covering the grape cuticle, which enhance the permeability of the grape skin and facilitate the moisture diffusion (Doymaz et al. 2002; Doymaz et al. 2012). These pretreatments consist of dipping the berries into alkaline emulsions of ethyl or methyl esters, sodium hydroxide and potassium carbonate during several minutes (Femenia et al. 1998; Doymaz et al. 2002; Bingol et al. 2012; Doymaz et al. 2012). Ethyl oleate reduces the resistance to moisture diffusion through the grape skin by dissolving the components of the epicuticular wax layer (Doymaz et al. 2002). Sodium hydroxide solutions solubilize large amounts of pectic substances and xyloglucans, whereas potassium metabisulfite solutions cause minor modifications in the composition of cell wall polysaccharides (Femenia et al. 1998). Postharvest ethylene treatment also induces cell wall degradation by activating enzymes (Botondi et al. 2011). Nevertheless, the preservation of the physical, chemical, nutritional and organoleptic characteristics of dehydrated grapes is desirable even when these pretreatments are used (Serratosa et al. 2012). Physical pretreatments can be as effective as the chemical methods for increasing the dehydration rate and permit safer dehydrated products to be produced, but the chromatic quality of physically treated grapes is worse than that of chemically treated grapes (Di Matteo et al. 2012).

The skin hardness of fresh berries influences the dehydration kinetics during postharvest withering. The grape dehydration rate significantly decreases with increasing skin hardness (Rolle et al. 2011a; Giacosa et al. 2012). The chemical pretreatment of the berries modifies the epicuticular wax layer and cell wall, which in turn affects the mechanical properties of fruits (Lara et al. 2014). Particularly in grapes, skin breakage and overall tissue softening are observed (Femenia et al. 1998). The concentration of chemical agent, dipping time and temperature are the most important factors in devising pretreatment strategies for postharvest dehydration.

Thermally processed biomaterials support a texture degradation closely related to enzymatic and nonenzymatic changes in the cell wall pectin (Chong et al. 2008). Therefore, the dehydration process also promotes texture changes in the fruit (Chong et al. 2008; Bolin and Huxsoll 1987; Rahman 2005), which depend on the dehydration rate (Bellincontro et al. 2009; Mencarelli et al. 2010; Xiao et al. 2010). Some studies showed a significant decrease in the instrumental texture parameters of winegrapes during the postharvest withering process under various controlled thermohygrometric conditions (Rolle et al. 2013). Furthermore, strong negative correlations were found between skin hardness and weight loss during withering (Rolle et al. 2013). Other researchers also indicated a softening effect induced by air drying (Bolin and Huxsoll 1987). Because skin hardness is basically determined by the vacuole turgidity, reduced cell turgor caused by water loss requires lower rupture force (De Belie et al. 1999). Conversely, Xiao et al. (2010) reported that high temperatures cause grape hardening during the postharvest dehydration process in a hot-air impingement dryer. A hard layer containing previously dissolved solutes is formed on the surface of the berry, probably as a consequence of a faster water removal rate from the surface than of the water migration rate from the interior (Bai et al. 2002). Muganu et al. (2011) also reported an increase in skin resistance to puncturing during grape postharvest dehydration.

No comprehensive study published up until now has systematically investigated the effect of alkaline pretreatment on the dehydration kinetics and rheological features of grapes used for wine production while an interesting study was carried out by Ramming (2009) on the dehydration behaviour of table grapes (Sumer Muscat, Diamond Muscat, Primus and Thompson Seedless) by using chloroform, rubbing and specific drying conditions. Therefore, the aim of this study was to evaluate the influence of the content of sodium hydroxide in the dipping solution and the dipping time on weight loss during the postharvest dehydration process of “Muscat of Alexandria” winegrapes, which originally were used as table grapes, under controlled thermohygrometric conditions. Furthermore, the relationships between different experimental conditions used for the chemical pretreatment and berry skin mechanical properties were investigated for the first time in this study. For this aim, during grape dehydration, the effect of the different dipping conditions on weight loss and skin mechanical properties was assessed using central composite design (CCD) and response surface methodology (RSM).

2. Material and methods

2.1. Grape sampling, alkaline pretreatment and dehydration process

In 2013, grape clusters of the Muscat of Alexandria cultivar (*Vitis vinifera* L.) were randomly sampled from various vines in an experimental vineyard located in the Mazara del Vallo (Tp) growing zone (Sicilia, South-West Italy). The sample consisted of about 15 kg of healthy grape berries. All of the berries in each cluster were manually separated from the stalk maintaining attached short pedicels, and they were sorted according to their density by flotation in saline solutions of different contents (from 100 to 190 g/L sodium chloride, corresponding to densities comprised between 1069 and 1125 kg/m^3) (Rolle et al. 2012). The presence of the pedicel prevents saline solution entry into the berry during flotation. This densimetric sorting allows obtaining more homogeneous samples and minimizing the possible ripening effect among berries. The study was carried out on the berries belonging to the three most representative classes with densities of 1081, 1088 and 1094 kg/m^3, which accounted for relative weights of about 55, 25 and 20% w/w, respectively. The sorted berries were washed with water and visually inspected; those with damaged skins were discarded. Forty-eight sets of thirty sorted berries each were randomly selected and placed on appropriate metallic supports with meshes of 0.64 cm^2 (0.8 x 0.8 cm), which were introduced into perforated boxes (60 x 40 x 15 cm, 6 metallic supports per box, 180 sorted berries per box) in a single layer for correct pretreatment and aeration. Each set contained the same relative weight of berries belonging to the three density classes as the original distribution. Sixteen pretreatment conditions were evaluated in agreement with the CCD experimental matrix (Table 1). The chemical pretreatment involved dipping the berries into a sodium hydroxide solution at 25 °C. On the basis of the conditions proposed by Vázquez et al. (2000), the sodium hydroxide content was 10, 20, 45, 70 or 80 g/L, and the dipping time was 10, 61, 185, 309 or 360 s. For each CCD experiment, three sets were treated. The treated berries were washed with water at 25 °C for 30 s and air dried. All sets were subjected to convective dehydration during thirteen days at a temperature of 30 °C, a relative humidity (RH) of 30% and an air speed of 0.9 m/s in a thermohygrometrically controlled chamber. These environmental conditions attempt to reproduce those usually used for dehydration of Muscat of Alexandria grapes in the Pantelleria island. Each set was individually weighed using a technical balance with a precision of 0.01 g (Gibertini E1700, Modena, Italy) to determine the weight of the fresh samples. In order to determine the dehydration kinetics, the weight was also accurately measured at different times during the dehydration process, and the weight loss percentage was calculated (Rolle et al. 2011a; Rolle et al. 2013) as:

$$\mathrm{WL\%} = 100 - \frac{\mathrm{W_d}}{\mathrm{W_f}} \times 100 \qquad (1)$$

where WL% is the weight loss percentage, W_d is the weight of dehydrated samples, and W_f is the weight of fresh samples.

2.2. Chemical analysis

Three replicates of twenty chemically untreated and undehydrated berries were analyzed, and three replicates of twenty dehydrated berries (experiments 9-11, central point) were analyzed at WL% of 35 (day 5), 50 (day 8) and 65 (day 13), locally referred 'Passolata', 'Bionda' and 'Malaga', respectively. Standard physicochemical parameters were determined in the grape juice obtained by manual crushing and centrifugation. Total soluble solids content (°Brix, as SSC) was measured with an Atago 0–32 °Brix temperature compensating refractometer (Atago Corporation, Tokyo, Japan). pH was determined by potentiometry using an InoLab 730 pHmeter (WTW, Weilheim, DE). Titratable acidity (g/L tartaric acid, as TA) was estimated using the International Organization of Vine and Wine method (OIV, 2008).

2.3. Instrumental texture analysis

In one of the three sets used for each CCD experiment, the berries were placed in the boxes in numbered positions, and skin mechanical properties were measured after chemical pretreatment and after dehydration to WL% of 65 (day 13). A TA.XTplus texture analyzer (Stable Micro Systems, Godalming, Surrey, UK), equipped with an HDP/90 platform and a 5 kg load cell, was used for skin texture analysis. The skin hardness was assessed by a puncture test using an SMS P/2N needle probe (Stable Micro Systems), a test speed of 1 mm/s and a penetration depth of 3 mm (Rolle et al. 2013; Letaief et al. 2008). Each berry was individually punctured in the lateral face, and two parameters were measured: skin break force as F_{sk} (N) and skin break energy as W_{sk} (mJ). The first variable corresponds to the skin resistance to the needle probe penetration, and the second variable is represented by the area under the force-time curve, which is limited between 0 and F_{sk} (Letaief et al. 2008). The use of a needle probe allows separate estimation of this skin mechanical characteristic, minimizing the possible interferences caused by the pulp firmness on the results. The microhole caused by the needle probe penetration was closed with a microdrop of natural resin to avoid interferences in the pretreatment and dehydration processes (Rolle et al. 2011a; Rolle et al. 2013). All data acquisitions were made at 500 points per second, and the skin mechanical properties were calculated from force-distance curves using the Texture Exponent software package (Stable Micro Systems).

2.4. Experimental design and statistical analysis

Two factorial 2^2 CCD was used to optimize the experimental conditions of the chemical pretreatment of winegrapes (Torchio et al., 2011). Independent variables were the sodium hydroxide content in the dipping solution (X_1) and dipping time (X_2), which were studied at five different levels (Table 1). The codified values for the variables ranged between +1.414 and −1.414, taking the zero value as central point. A total of 16 experiments including three replicates of the central point, four treatments to increase the robustness (minimum and maximum values of the two independent variables) and one experiment corresponding to chemically untreated samples (immersed in water for

1 min) were carried out. The mean values of replicates were adjusted to the following second-order polynomial model (Vázquez et al. 2000):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \qquad (2)$$

where Y is the response variable, X_1 and X_2 correspond to the independent variables, b_0 is the value in the central point conditions, b_1 and b_2 represent the principal effects associated with each variable, b_{11} and b_{22} are the squared effects and b_{12} is the interaction effect. Surface plots were represented from the regression models obtained using RSM. A statistical analysis was performed to fit the response to second-order polynomial models using regression analysis, including the Durbin-Watson statistic to test the randomness of the residuals.

One-way analysis of variance (ANOVA) was used in order to establish statistical differences in the grape chemical composition due to berry dehydration. All statistical analyses were performed using the software package Statistics version 7.0 (Statsoft Inc., Tulsa, OK, USA).

3. Results and discussion

3.1. Dehydration kinetics

Significant changes in the dehydration kinetics were found among berries differently pretreated with sodium hydroxide. Therefore, it is important to assess the effects of the two independent variables involved in the effectiveness of the chemical pretreatment used (sodium hydroxide content and dipping time) on the dehydration kinetics of berries. The effect of the sodium hydroxide content became more important as dehydration progressed, whereas the increased effect of the dipping time was not so evident. Figure 1 shows the relationship between WL%, sodium hydroxide content and dipping time at different days during the dehydration process, which is illustrated by a three-dimensional representation of the response surface. The Muscat of Alexandria cultivar evidenced an average WL% of 65.2 after thirteen days of withering at 30 ºC and 30% RH, which corresponded to a daily average WL% ranging from 8.6 (between the second and first day) to 2.6 (between the thirteenth and twelfth day). The average WL% was 46.2 in the first seven days, whereas it was 19.0 in the remaining six days. The dehydration rate was not constant during the dehydration process, and it decreased with increasing the dehydration time. The equations of the two curves corresponding to the slowest and fastest dehydration processes (unpretreated berries and berries pretreated with 80 g/L of sodium hydroxide for 360 s, respectively) were $Y = 0.2165X^2 – 7.5756X + 99.451$ ($R^2 = 0.9996$) and $Y = 0.2709X^2 – 8.5612X + 99.491$ ($R^2 = 0.9997$), respectively, where X are dehydration days and Y is WL (%). Indeed, the drying process presents three classical steps: the initial one where the product temperature and water vapor pressure increase and so the drying rate increases, a second step where the drying rate is constant and the third step where it declines because the water in the liquid phase forms liquid bridges inside the porous solid (Barbosa de Lima et al. 2015). Factors such as sugar accumulation can hinder the moisture diffusion through the berry skin (Vázquez et al. 2000) and, furthermore, the grape shrinkage can slow down the dehydration process because of a decrease in porosity (Gabas et al. 1999). Anyway, the finding of significant differences in the water loss between berry sizes and not between Brix indicates that berry sugar level has a minimum effect on the ability of the water to move through the berry compared to the effect of the surface area on water movement (Ramming 2009).

The dehydration kinetic was influenced by the berry pretreatment applied (Figure 1). After two days of dehydration, the values of WL% increased with increasing either the dipping time or the sodium hydroxide content. Nevertheless, the time effect was more accused. The combined use of long times and high sodium hydroxide contents during the berry pretreatment showed lower values of WL% in relation to the individual use of them. At the fifth day of dehydration, the trend was similar to that observed in the second day. However, at the fifth day, the difference between the effects of the two independent variables was smaller, and the combined use of long times and high sodium hydroxide contents caused a lower decrease in the values of WL% respect to their individual use. Therefore, the berry pretreatment with low sodium hydroxide contents (10-20 g/L) facilitated the dehydration process during the first five days when dipping times longer than 5 min were used.

From the seventh day of dehydration, at which time the average WL% was close to 50, the highest values of WL% were obtained using intermediate sodium hydroxide contents and dipping times (around 45 g/L and 185 s, respectively). The effects of the two independent variables on WL% were attenuated or even inversed particularly when dipping times longer than 250 s and sodium hydroxide contents higher than 70 g/L were used.

In the case of grape pretreatments with sodium hydroxide, the dehydration rate increases due to the creation of fissures in the skin (Femenia et al. 1998; Azzouz et al.

2002), which constitute preferential pathways through which water can diffuse more easily and cross the initially impermeable epicuticular wax layer. Indeed, it is known that epicuticular wax is the main protection against water loss, and its removal by rubbing or chloroform increases the water loss (Ramming 2009). In fruits, Veraverbeke et al. (2003) demonstrated that the moisture diffusion coefficient of wax is at least hundred times smaller than that of cutin. Barbanti et al. (2008) also justified the lower moisture diffusion coefficients obtained, in relation to others reported for dehydrated grapes (1–2 orders of magnitude), by the use of unpretreated berries. Furthermore, pectic polysaccharides and hemicellulosic xyloglucans are solubilized, and the esterification degree of pectic substances decreases probably as a result of structural modifications within the fiber matrix (Femenia et al. 1998). However, these fissures may undergo progressive closure as the grape shrinks and sugars migrate to the skin (Vázquez et al. 2000; Azzouz et al. 2002). Therefore, the effects of the pretreatment with sodium hydroxide on the dehydration kinetics are largely limited to the beginning of the dehydration process when a significant grape shrinkage and sugar accumulation in the skin have not yet occurred. In the present work, although low sodium hydroxide contents were enough to facilitate water loss during the first five days of dehydration, from the seventh day onwards (WL% $\geq$ 50), berries pretreated with higher contents of sodium hydroxide showed higher dehydration rates probably due to the presence of larger fissures that were more difficult to occlude. In fact, the use of intermediate sodium hydroxide contents and dipping times (around 45 g/L and 185 s, respectively) permitted to achieve WL% of 65.

Table 2 shows the second-order polynomial models obtained for WL% at different times (2, 5, 7, 9, 11 and 13 days) during the dehydration process. The lack-of-fit parameter was not significant ($p > 0.02$), and from the second day onwards the mathematical equations obtained explained at least 64% of the variability in the response. Taking into account that a value of the Durbin–Watson statistic close to 2.0 indicates a weak correlation or random distribution of residuals (Rutledge and Barros 2002), the regression residuals found at day 2, 5, 9 and 13 were not correlated. Therefore, the most satisfactory models (goodness-of-fit) were found at day 5 and 13 with determination coefficients (R^2) higher than 0.75, *p*-values less than 0.01 and values of the Durbin–Watson statistic converging to 2. The two independent variables had almost exclusively linear effects on WL%, and the interaction effect was very small.

3.2. Instrumental texture analysis

The changes in the mechanical properties defining skin hardness (F_{sk} and W_{sk}) were significantly different during dehydration for berries differently pretreated with sodium hydroxide. Figure 2 shows the effects of both the sodium hydroxide content and dipping time on the variation of skin break force (ΔF_{sk}) and skin break energy (ΔW_{sk}) after pretreatment and after dehydration up to WL% of 65. The highest positive values of ΔF_{sk} and ΔW_{sk} corresponded to the greatest sodium hydroxide contents and longest dipping times. Conversely, the highest negative values of ΔF_{sk} were associated with a dipping time of 10 s and sodium hydroxide contents between 45 and 80 g/L, as well as with times longer than 10 s but reducing the upper limit of the content range of sodium hydroxide up to 45 g/L for 250 s. Moreover, the lowest values of ΔW_{sk} were obtained for intermediate sodium hydroxide contents and dipping times.

The trends of ΔF_{sk} and ΔW_{sk} with the increase in the dipping time were different depending on the sodium hydroxide content. In fact, the values of ΔF_{sk} and ΔW_{sk}

increased with increasing the dipping time when the greatest sodium hydroxide contents were used, whereas the inverse tendencies were observed for the lowest contents. At any dipping time, the values of ΔF_{sk} and ΔW_{sk} initially decreased with increasing the sodium hydroxide content and then increased for contents higher than 45 g/L. However, the decreasing effect was more evident for shorter dipping times, whereas the increasing effect was more pronounced for longer times. It is important to take into account that the effects of the two independent variables on the response were more accused for ΔW_{sk} than for ΔF_{sk}.

Some studies highlighted that the faster water evaporation causes the quicker cell turgor loss and texture degradation, and therefore skin hardness decreases (De Belie et al. 1999). During grape dehydration under controlled thermohygrometric conditions, skin hardness is strongly and negatively correlated with weight loss (Rolle et al. 2013). This agrees with the largest decrease observed in the values of F_{sk} and W_{sk} when the berries were pretreated with intermediate sodium hydroxide contents and dipping times, for which the highest values of WL% were obtained at the end of the dehydration process. Conversely, the occurrence of a significant grape shrinkage and the formation of a hard layer in the skin due to the sugar migration and cell layers compactness could explain the highest skin hardening (according to increased F_{sk} and W_{sk}) when the berries were pretreated with the greatest sodium hydroxide contents during the longest dipping times. Other researchers also reported increased skin resistance to puncturing during postharvest dehydration of grapes (Muganu et al. 2011) and other fruits (Contreras et al. 2008).

The model explained 82% of all variance of the results obtained for ΔF_{sk} and 71% for ΔW_{sk}, and the lack-of-fit parameter was not significant ($p > 0.01$). However, the value of the Durbin-Watson statistic showed that the regression residuals were too correlated for ΔW_{sk}, and therefore this skin mechanical property could not be satisfactorily predicted by the RSM model. The mathematical equations obtained and statistical parameters are summarized in Table 2. The two independent variables had only linear effects on the responses.

Skin hardness is variety dependent (Giacosa et al. 2014) and, within the same variety, the growing area and season heavily influence skin hardness (Torchio et al. 2010; Río Segade et al. 2011). Particularly some climatic indices are significantly correlated with skin break force as a consequence of the genotype–environment interaction (Sato et al. 2000; Rolle et al. 2011b). Because the skin hardness of fresh berries is an important variable in the management of the dehydration kinetics (Giacosa et al. 2014; Rolle et al. 2011a), fresh grapes with different skin hardness may require different pretreatment conditions (sodium hydroxide content and contact time) to achieve the same dehydration grade. Furthermore, some researchers reported undesirable changes in the color, aroma and flavor of chemically treated berries compared with those untreated, but these changes depend on the pretreatment applied (Bingol et al. 2012; Doymaz et al. 2012; Serratosa et al. 2012). Therefore, the knowledge of the best pretreatment conditions to achieve a given dehydration grade while preserving the quality attributes of winegrapes would be greatly appreciated by winemakers.

3.3. Chemical analysis

SSC increased significantly during the dehydration of berries pretreated with sodium hydroxide because of the concentration of the juice components, particularly sugars (Table 3). According to the dehydration kinetics, sugars were concentrated faster at the beginning of the withering process, and the concentration rate decreased as dehydration progressed. The values of pH and TA did not vary significantly during the dehydration process, with the exception of TA at WL% of 35. The initial decrease in TA was likely due to malic respiration (Rolle et al. 2013; Bellincontro et al. 2004), but this malic acid loss was then masked by the concentration effect of malic and tartaric acids related to weight loss.

Some researchers have reported that TA and SSC are strongly and positively correlated with WL% during the postharvest dehydration process under controlled thermohygrometric conditions (Rolle et al. 2013). In the present study, these relationships were not significant probably due to the pretreatment of the berries and the higher values achieved of WL%.

4. Conclusions

By using postharvest sodium hydroxide pretreatment of grape berries, the strongest dehydration was not obtained using the highest content and the longest contact time, but these two variables should be selected as a function of the cultivar, dehydration conditions and the rate of water loss desired. This study contributes to increase the knowledge on the impact of two important pretreatment factors (sodium hydroxide content and dipping time) on the grape dehydration kinetics. The results showed that the use of relatively low sodium hydroxide contents permits to increase the dehydration rate. This is a beneficial aspect because of the reduced risk of residues remaining on the surface of the berries and a better environmental sustainable of the pretreatment process. The pretreatment conditions also influenced skin mechanical properties, and the skin hardness of dehydrated grapes could be satisfactorily predicted from the sodium hydroxide content and dipping time used during the berry pretreatment with the equations proposed. The prediction of skin hardness is of great importance because it may affect the extractability of phenolic compounds during maceration. The knowledge of the best pretreatment conditions to achieve a given dehydration grade, while preserving the quality attributes of grapes, provides useful information for improving the final product through a better management of the alkaline pretreatment and dehydration processes.

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Table 1
Experimental matrix of CCD.

Experiment	Sodium hydroxide content (coded value) (x_1)	Time (coded value) (x_2)	Sodium hydroxide content (real value) (X_1, g/L)	Time (real value) (X_2, s)
1	-1	-1	20	61
2	1	-1	70	61
3	-1	1	20	309
4	1	1	70	309
5	-1.4141	0	10	185
6	1.4141	0	80	185
7	0	-1.4141	45	10
8	0	1.4141	45	360
9	0	0	45	185
10	0	0	45	185
11	0	0	45	185
12	-1.4141	-1.4141	10	10
13	-1.4141	1.4141	10	360
14	1.4141	-1.4141	80	10
15	1.4141	1.4141	80	360
16	-	-	0	0

Table 2

Second-order polynomial model by central composite design (CCD) for weight loss and variation of skin mechanical properties during dehydration in berries pretreated with sodium hydroxide.

Parameter	Day	Equation	R^2	*p*	D-W
WL (%)	2	$Y = 14.7026 + 0.0469X_1 + 0.0160X_2 - 0.0002X_1^2 - 0.0002X_1X_2 - 1.69E\text{-}5X_2^2$	0.57	0.020	1.860
	5	$Y = 32.0685 + 0.0729X_1 + 0.0225X_2 - 0.0002X_1^2 - 0.0003X_1X_2 - 1.98E\text{-}5X_2^2$	0.76	0.009	2.149
	7	$Y = 41.0016 + 0.1399X_1 + 0.0219X_2 - 0.0010X_1^2 - 0.0002X_1X_2 - 2.54E\text{-}5X_2^2$	0.88	0.001	1.259
	9	$Y = 47.9143 + 0.1721X_1 + 0.0273X_2 - 0.0013X_1^2 - 0.0002X_1X_2 - 4.23E\text{-}5X_2^2$	0.64	0.006	2.223
	11	$Y = 56.3782 + 0.1862X_1 + 0.0265X_2 - 0.0014X_1^2 - 0.0002X_1X_2 - 4.18E\text{-}5X_2^2$	0.72	0.004	3.021
	13	$Y = 58.3249 + 0.1995X_1 + 0.0280X_2 - 0.0016X_1^2 - 0.0001X_1X_2 - 4.72E\text{-}5X_2^2$	0.80	0.001	1.690
ΔF_{sk} (N)	13	$Y = 0.1101 - 0.0220X_1 - 0.0017X_2 + 0.0002X_1^2 + 2.79E\text{-}5X_1X_2 + 1.68E\text{-}6X_2^2$	0.82	0.002	1.885
ΔW_{sk} (mJ)	13	$Y = 0.9439 - 0.0437X_1 - 0.0039X_2 + 0.0004X_1^2 + 4.45E\text{-}5X_1X_2 + 6.08E\text{-}6X_2^2$	0.71	0.005	0.876

WL: weight loss; ΔF_{sk}: variation of skin break force during dehydration; ΔW_{sk}: variation of skin break energy during dehydration; X_1: sodium hydroxide content (g/L); X_2: dipping time (s); R^2: determination coefficient; D-W: Durbin-Watson statistic.

Table 3
Standard physicochemical parameters during dehydration of berries pretreated with sodium hydroxide.

WL (%)	SSC (ºBrix)	pH	TA (g/L as tartaric acid)
0	22a	3.20a	5.40b
35	31b	3.26a	3.97a
50	40c	3.25a	5.15b
65	45d	3.24a	5.25b

All data are expressed as average value (n = 3).
Different Latin letters within the same column indicate significant differences among different dehydration levels (Tukey-b test; $p < 0.001$).
WL: weight loss; SSC: Total soluble solids content; TA: titratable acidity.

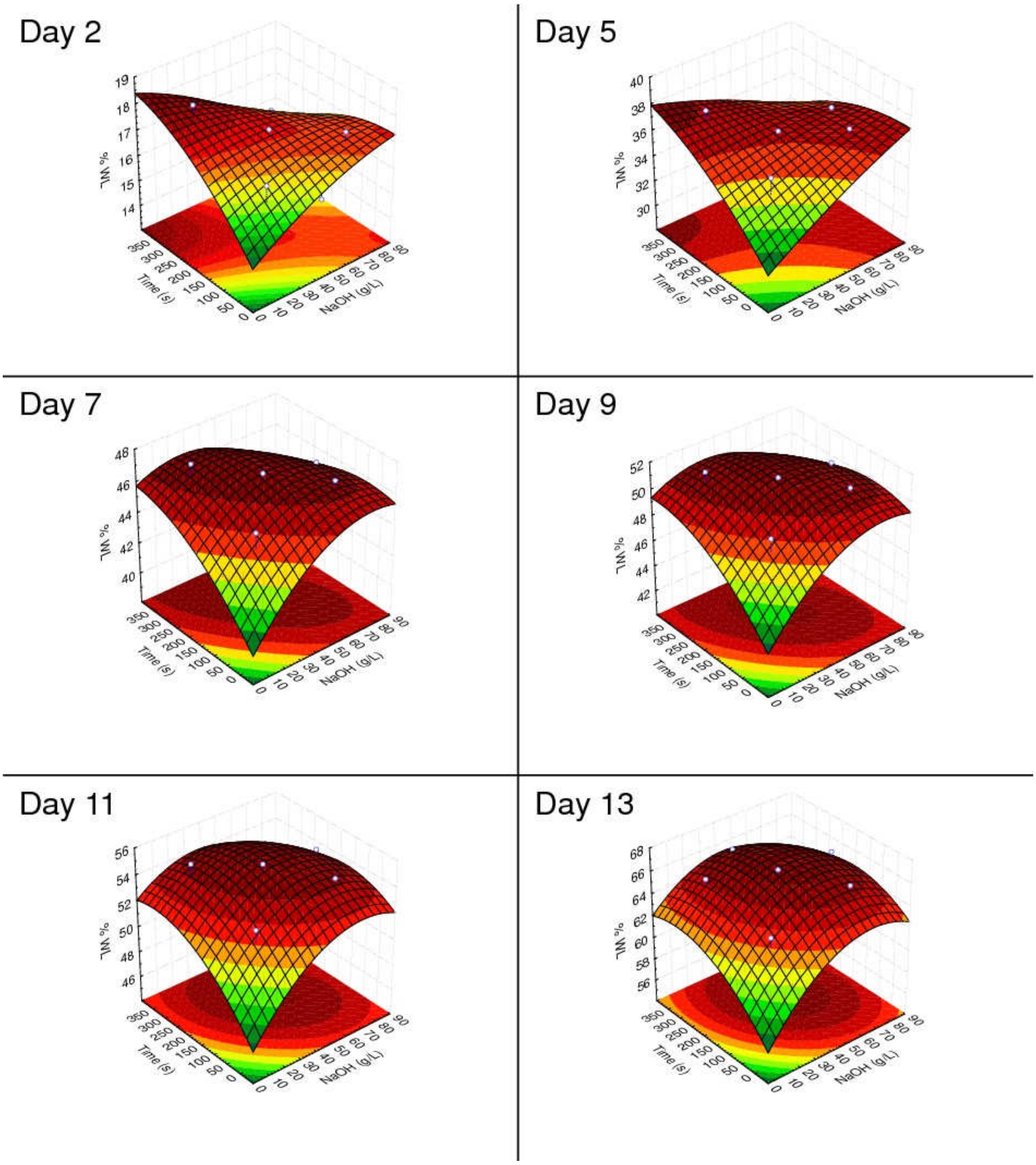

Figure 1. Assessment with Response Surface Methodology the effect of alkaline pretreatment on berry weight loss during the dehydration process.

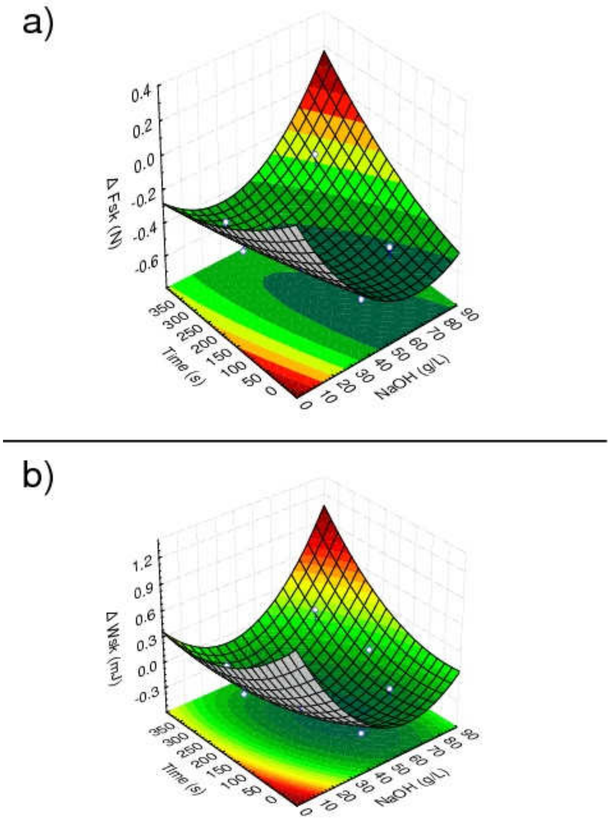

Figure 2. Assessment with Response Surface Methodology the effect of alkaline pretreatment on the changes in mechanical properties with dehydration: the variation of berry skin break force (a) and energy (b).