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Comparison of foliar spraying and soil application of calcium and potassium sulfate fertilizers on some chemical and mechanical properties of Lal grape

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ABSTRACT

Direct application of agricultural fertilizers to the soil is a traditional method for increasing fruit tree yield, but most fertilizers may leach from the soil or form insoluble compounds. Foliar application of fertilizers is one of the effective methods to increase product quality and reduce fertilizer costs. In order to compare direct calcium and potassium fertilization with foliar application on the yield and quality of the Lal grape variety, an experiment was conducted in a randomized complete block design with 6 treatments in 4 replications in one of the orchards of Shahrood city. The treatments included control (C), 1 kg of biochar from grape pruning residues (BC),100 grams of potassium sulfate fertilizer for each vine (FK), 100 grams of calcium sulfate fertilizer for each vine (FCa), foliar spraying of 10 grams of potassium sulfate (SK), and 10 grams of calcium sulfate for each vine (SCa) at 5 growth stages. At the end of the experiment, total soluble solids (TSS), total acidity, and pH of the fruit juice were measured, and calcium, potassium, sodium, and phosphorus in grape berries and their firmness were determined by a material testing machine. The highest and lowest fruit phosphorus levels were found in the control treatment and the calcium-containing treatments (FCa, SCa), respectively. All treatments except SK significantly increased fruit calcium. The highest amount of fruit calcium was observed in FCa and then SCa treatments, which increased by 2.77 and 2.35 times, respectively, relative to the C. The biochar (BC) treatment increased fruit calcium by about 30%. FK treatments showed the highest potassium amount and firmness (0.3215 N/mm^2). Although foliar application of fertilizers had less effect on fruit firmness and brittleness than soil application, it reduced the fertilizer consumption by 90 percent, when compared to the soil application. The highest flexibility and brittleness of the berries were found in the FCa treatment. To increase the firmness and brittleness of the fruit and consequently increase its marketability and shelf life, the combined use of potassium and calcium fertilizers is suitable.

Highlights

- Soil application had a better effect on calcium uptake than foliar application of fertilizers.
- Potassium fertilization had the greatest effect on grape berry firmness.
- Calcium fertilization made grape berries more flexible.
- To increase grape shelf life, combined application of calcium and potassium is recommended.

1. Introduction

Grapes are one of the most important crops adapted to dry regions worldwide (Gambetta, 2020). This product is considered one of the most popular and favorite fruits in the world due to its excellent taste and aroma. This fruit has a high nutritional value, containing sugar in the form of monosaccharides (glucose and fructose) and various phenolic compounds (Kandylis et al., 2021). Grapes also contain minerals such as potassium, magnesium, iron, and calcium, and some vitamins such as vitamins C, B_{12}, and B_6, which are nutritionally important (Conde et al., 2015; Kandylis et al., 2021). The Lal grape is native to

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Afghanistan and is considered one of the favorite grapes for fresh consumption, and therefore its crispness and firmness are of particular importance for marketability. This grape is a type of white grape with large seeds and is very sweet. Various factors affect its quality, including climatic factors, soil type, and agricultural management. Among these factors, achieving nutritional balance will have an important impact on fruit quality (Rasouli et al., 2014).

The use of organic fertilizers is one of the traditional methods for providing the nutrients needed by trees, in which the nutrients are gradually released, thereby improving the nutritional conditions of the trees. Organic fertilizers also improve the physical, biological, and chemical properties of the soil. Most importantly, the use of organic fertilizers minimizes the side effects of mineral fertilizers on the environment and preserves other living organisms needed in sustainable agriculture (Lazcano et al., 2020). Among these organic compounds, biochar can be mentioned, which, due to its long persistence in the soil, improves the physical, chemical, and biological properties of soils, especially heavy clay soils. Much research has been conducted on the positive effect of biochar on plant growth and nutrition (Abbaspour et al., 2020; Karimian et al., 2022; Keykhosravi et al., 2020).

In order to improve the quality of agricultural products, it is necessary to use some nutrients at a specific time of plant growth; therefore, the use of specific chemical fertilizers at a specific time and for some products is necessary. In this regard, to improve the efficiency of fertilizers and increase crop yield, foliar spraying of fertilizers on the aerial parts of plants during the growing season might have better results than their direct application to the soil (Azizi et al., 2017; Minazadeh et al., 2018; Swathi et al., 2019).

Foliar spraying of nutrients on the aerial parts of grapevines has many advantages for economic and environmental reasons. This can improve the efficiency of nutrient absorption because nutrients are directly absorbed by the leaves. Foliar spraying provides specific nutrients at critical stages of growth such as budding, flowering, and grape fruit set promptly (Mohebbi et al., 2022).

Potassium is an essential nutrient for plants, being the most abundant cation in grape berries. It plays a key role in the balance of electrical charge and sugar transport. Potassium also increases total soluble solids (TSS), early fruit ripening, and resistance to diseases. It also affects fruit firmness, which increases its storage properties (Griesser et al., 2017). Under conditions of potassium deficiency, leaves fall before maturity, delaying fruit ripening and severely reducing yield (Griesser et al., 2017; Rogiers et al., 2017).

Calcium, as an essential nutrient, plays a key role in the strength of the fruit cell wall. Foliar application of calcium increases sugar, anthocyanin, and total phenols in the fruit (Wang et al., 2019). Deficiency of this element may cause incomplete flowering, short branched roots, leaf chlorosis, and cluster necrosis. Various studies have been conducted on the application of calcium on grape quality. Most researchers have pointed out the positive effect of calcium on grape quality and longer shelf life (Wang et al., 2019), while others did not observe a significant difference in grape quality, such as firmness, due to calcium application (Wang et al., 2019). This disagreement may be due to the timing of fertilization and its application. However, foliar application of calcium during the growing season may have different efficacy compared to direct application of this nutrient to the soil. Abbasi et al. (2020) found that spraying calcium chloride at 4 levels of 0, 0.5, 0.75, and 1% at intervals of 15 days from fruit set to grape harvest increased the yield and quality of grape berries.

Among the various grape varieties, Lal grapes are one of the grapes that have received attention for fresh consumption. The reason for its high marketability is mainly due to the crispness and firmness of its berries. For fresh consumption, mechanical properties are one of the most important parameters determining grape quality (Poposka et al., 2023). Therefore, the objectives of this study are to investigate the effect of soil application and foliar spraying of potassium and calcium on the absorption of these two nutrients by grape vines and to compare these two fertilization methods on the firmness and crispness of grape fruit.

2. Materials and methods

This study was conducted in a private vineyard located in Qaleh Shokat village, Shahrood city. Some properties of the soil is given in Table 1. To compare the effects of direct calcium and potassium fertilization versus foliar application on the yield and quality of Lal grapes about seven years old, an experiment was conducted in a randomized complete block design with 6 treatments and 4 replications. The treatments included control (without the use of potassium or calcium fertilizers; C), biochar from grape pruning residues (1 kg dry weight per vine; BC), potassium sulfate (K_2SO_4) fertilizer (100 g per vine; FK), calcium sulfate ($CaSO_4$) fertilizer (100 g per vine; FCa), potassium sulfate foliar spraying (10 g per vine in 5 growth stages; SK), and calcium sulfate foliar Spraying (10 g per vine in 5 growth stages; SCa). Grape pruning residues were used to prepare biochar (Keykhosravi et al., 2020).

Table 1. Some physical and chemical properties of the soil studied

Properties	Unit	Soil
pH		7.32
Electrical conductivity (EC)	dS/m	4.42
Clay	%	7
Silt	%	56
Sand	%	37
Organic matter	%	1.39
Lime	%	14.3

pH and EC of the soil in saturated paste extract, soil texture by hydrometer, organic matter by wet digestion method, and lime by acid neutralization method were measured (Sparks et al., 2020). All treatments received diammonium phosphate fertilizer before the growing season. Potassium or calcium fertilizers were added to the respective treatments before the growing season and mixed thoroughly with the soil. Potassium or calcium sulfates were sprayed 5 times after grape harvest in late October of the previous year, during the initial growth of leaves in early April (Bud burst), the bloom stage in early May, the unripened berries stage in early June, and before fruit ripening (Veraison) in late June (Parthiban et al., 2022). In each stage, 2 grams of potassium or calcium sulfate was dissolved in 1 liter of water and sprayed on the foliage of the mentioned treatments with a hand sprayer. At the time of harvest, grape berries were removed from all treatment replicates. Thus, the number of samples collected was 24. Each sample was divided into two parts. Part of the samples was dried for chemical analysis, and the other part was stored in the refrigerator for mechanical analysis and some other quality properties of the fruit. In fresh samples, the concentration of total soluble solids (TSS) was measured with a refractometer, total acidity by titration with sodium hydroxide, and the pH of the fruit juice was measured using a pH meter (Haridy et al., 2020).

All measurements were performed in 4 replications and at room temperature. In order to determine the mechanical properties of grape berries, a materials testing machine manufactured by SANTAM Company (STM-20) in Iran was used. The test was performed on 24 grape berries using a probe (diameter 5 mm and length 16.5 mm) with a constant displacement speed of 50 mm/min and a displacement length of 10 mm. The materials testing machine is shown in Figure 1.

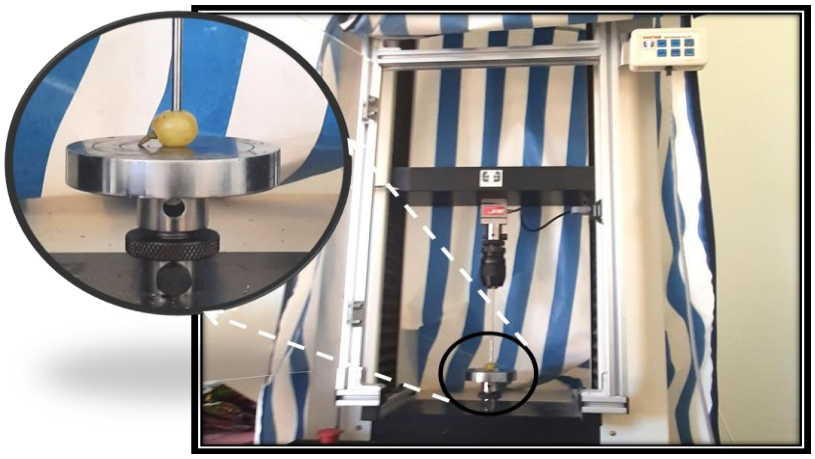


Figure 1. Image of the SANTAM device for determining the mechanical properties of grape berries.

Four parameters of fracture stress, fracture strain, fracture energy, and elastic modulus were determined from the force-displacement data.

$$\sigma_F = \frac{F_{Max}}{A} \quad (1)$$

$$\varepsilon_F = \frac{\delta_{Max}}{L_0} \quad (2)$$

$$\text{Energy} = \int_0^{\delta_{F_{Max}}} F d\delta = \sum_1^i (F_i + F_{i+1})(\delta_{i+1} - \delta_i)/2 \quad (3)$$

$$Module = \frac{\sigma_F}{\varepsilon_F} \quad (4)$$

In Equation 1, σ_F is the fracture stress (MPa), F_{Max} is the maximum force, and A is the cross-sectional area of the probe. In equation 2, ε_F is the strain at the fracture point, δ_{Max} is the change in length at the maximum force, and L_0 is the initial length of the grape berry. In equation 3, the energy is determined by calculating the area under the force-displacement diagram by numerically solving its integral. In equation 4, the elastic modulus is determined from the ratio of the fracture stress to the strain at the fracture point.

The concentrations of phosphorus, potassium, sodium, and calcium elements in the berries were measured. In this way, after oven-drying the sample at 70 ° C, it was crushed in a porcelain crucible, and after digestion by dry burning, the concentrations of the aforementioned elements in the samples were measured (Sparks et al., 2020).

In the samples, the phosphorus concentration was measured by spectrophotometry, the sodium and potassium concentrations were measured using a flame photometer, and the calcium concentration was measured using an atomic absorption spectrophotometer. The data mean was compared using SPSS software ver. 16 using Duncan's test and statistically analyzed at a probability level of 5%, and graphs were drawn using Excel software.

3. Results and discussion

3.1. Effect of treatments on chemical properties of berry

The analysis of variance (Table 2) indicates that the effect of treatments on pH, total acidity (TA), total soluble solids (TSS), and sodium concentration in grape berries was not significant at the 5% probability level, but it was significant on the concentration of calcium, potassium, and phosphorus in the berries at the 1% probability level.

Table 2. The analysis of variance related to the effect of treatments on some parameters measured in grape berries.

Source of variation	Df	Mean square						
		pH	TA	TSS	Ca	Na	K	P
Block	3	0.043 ns	0.008 ns	2.436 ns	0.002 ns	0.000 ns	0.114 ns	0.001 ns
Treatment	5	0.012ns	0.002ns	2.028ns	0.575**	0.000 ns	2.253 **	0.021**
Error	15	0.011	0.005	5.097	0.013	0.000	0.134	0.000
CV%		4.074	2.122	1.192	2.674	1.338	1.859	1.222

ns: not significant; * and ** significant at the 5% and 1% levels, respectively.

Comparisons of the treatment means (Figure 2) showed that all treatments except SK treatment significantly increased fruit calcium concentration compared to the control. The highest fruit calcium concentration was observed in FCa and then SCa treatments, which increased the amount by 2.77 and 2.35 times compared to the control, respectively. The treatment containing biochar (BC) increased fruit calcium concentration by about 30 percent compared to the control. Biochar, due to having nutrients such as calcium on its surfaces and their absorption by plant roots, causes better plant growth (Keykhosravi et al., 2020; Rafique et al., 2020). The FK treatment also significantly increased fruit calcium compared to the control. The better growth of this treatment is probably due to the addition of potassium, which caused the absorption of other nutrients, including calcium. Regarding potassium concentration, it should be noted that only FK and SK treatments were able to increase fruit potassium concentration by 54 and 46 percent, respectively, compared to the control. Naturally, the application of potassium, whether as a foliar spray or through soil application, increases its absorption by plants (Azizi et al., 2017; Karimi et al., 2021; Rogiers et al., 2017).

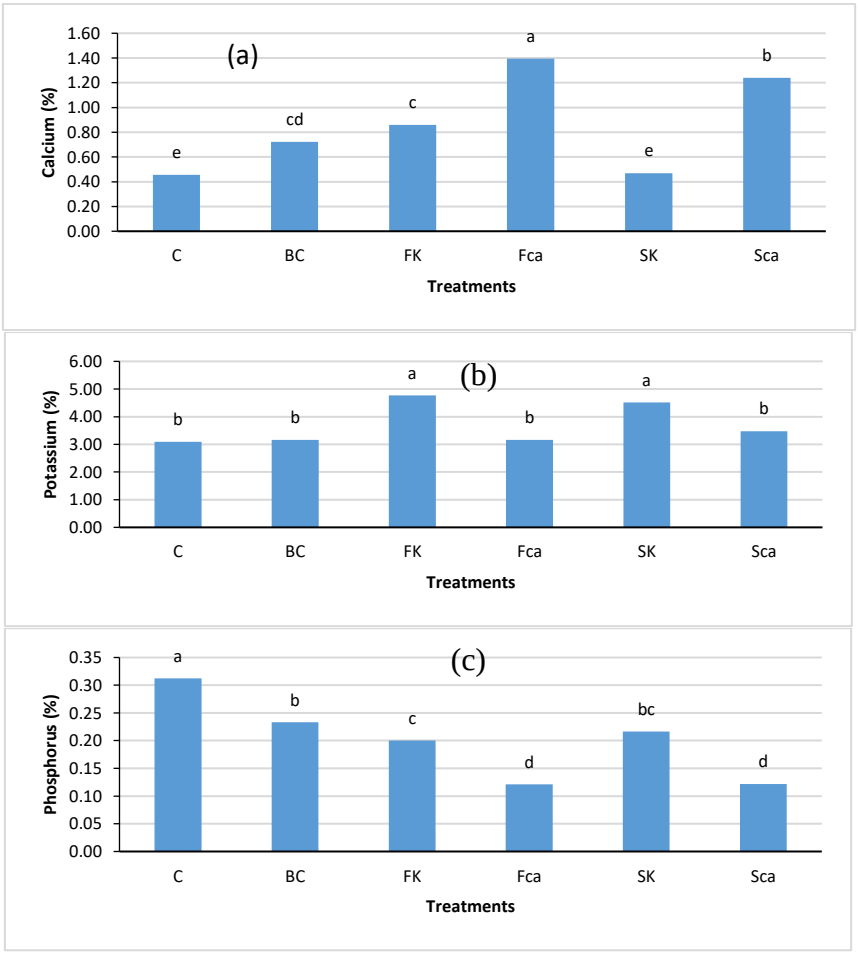


Figure 2. Effect of treatments on the concentration of calcium (a), potassium (b), and phosphorus (c) in grape berries. Control (C), biochar (BC), potassium fertilization (FK), calcium fertilization (FCa), potassium foliar spraying (SK), calcium foliar spraying (SCa). Columns with the same pattern, indicated by lowercase letters, are not significant at the 5% probability level based on Duncan's test.

The highest and lowest fruit phosphorus concentrations were observed in the control treatment and calcium-containing treatments (FCa, SCa), respectively. It seems that calcium and phosphorus have a negative interaction in their absorption by plant roots and their transport within the plant. The application of phosphorus-containing fertilizers to soils with high calcium, such as calcareous and gypsum soils, causes precipitation and inactivation of phosphorus in the soil, thereby reducing its absorption by plant roots (Kumar et al., 2021; Palani and Raju, 2019).

3.2. Effect of treatments on mechanical properties of berry

Only the analysis of variance related to modulus was significant at the 5% level, and other mechanical parameters were significant at the 1% level (Table 3).

Table 3. Analysis of variance related to effect of treatments on some mechanical properties of grape berries

Source of variation	Df	Mean square			
		Strain	Module	Stress	Energy
Block	3	0.002 ns	0.026 ns	0.000 ns	11.752 ns
Treatment	5	0.022**	0.258*	0.013**	39.669**
Error	15	0.004	0.025	0.002	21.914
CV%		18.70	22.51	22.25	33.76

ns: not significant; * and ** significant at the 5% and 1% levels, respectively.

Figure 3 shows the effect of different treatments on the mechanical strength of grape berries. The highest fracture stress (Figure 3a) was shown by the FK treatment with a tolerance of 0.3215 N/mm^2 (MPa). The other treatments had statistically the same fracture stress. It should be noted that the FK treatments had the highest potassium concentration in grape berries, which indicates the effect of the nutrient potassium on fruit firmness. It seems that the accumulation of potassium in grape berries makes the berry skin more resistant to fracture stress. Various studies have proven the accumulation of potassium in the skin compared to the fruit flesh (Griesser et al., 2017; Ramos and Romero, 2017).

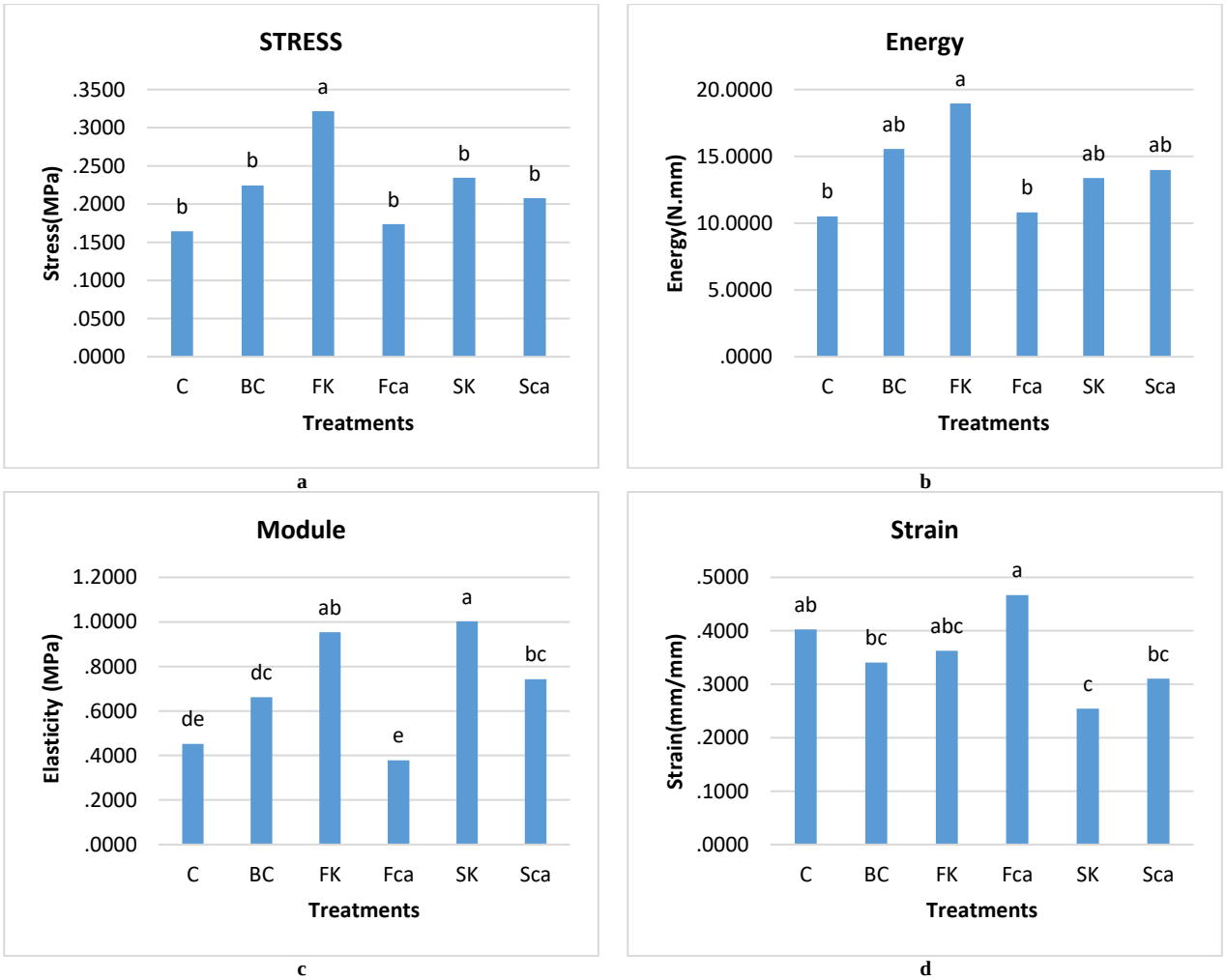


Figure 3. Effect of treatments on fracture stress (a), energy (b), modulus of elasticity (c), and fracture strain (d) in grape berries. Control (C), biochar (BC), potassium fertilization (FK), calcium fertilization (FCa), potassium foliar spraying (SK), calcium foliar spraying (SCa). Columns with the same pattern, indicated by lowercase letters, are not significant at the 5% probability level based on Duncan's test.

The fracture energy factor indicates the elasticity of the tissue. The highest energy stored in grapes was observed in FK, which indicates the fact that this treatment requires more energy to fracture; therefore, it increased the fruit firmness.

Another parameter related to the slope of the stress-strain line is defined as the modulus of elasticity. FK and SK treatments had the highest values, which is probably due to the hardness and brittleness of the grape skin. The softest tissue was shown by FCa and C treatments.

Strain indicates the deformation before failure, which was observed to be the most flexible in the FCa treatment and the least flexible and brittle in the FK treatment. Overall, the results show that the calcium-containing treatment made the grape berry tissue softer and more flexible, while the potassium-containing treatment made

the tissue firmer but more brittle. Various studies have shown that potassium fertilization alone can affect fruit firmness. For example, da Silva et al. (2024) observed an increase in the firmness of Syrah grape berries using different amounts of potassium fertilizers. However, calcium fertilization may be required to reduce grape berry fragility and brittleness (Obenland et al., 2015; Rogiers et al., 2017). However, the interactions between potassium and calcium and their effect on fruit firmness and brittleness depend greatly on the time of fertilization, harvest time, and grape variety (Rogiers et al., 2017). For example, in the research of Poposka et al. (2023), during 3 years of foliar spraying of nitrogen and calcium on Cardinal grape vines in 4 growth stages of the vines (before and after flowering, fruit formation, and grape berry coloring), it was shown that the highest pressure resistance and breaking resistance were observed in treatments containing calcium foliar spraying. Swathi et al. (2019) also investigated the effect of foliar spraying of 10 different treatments at two growth stages (45 days after pruning and 10 days after the first foliar spraying) on grape berry firmness (Paneer variety). Among the treatments, calcium foliar spraying with boron had the best results compared to the control and to foliar spraying of each of these nutrients alone. They did not observe a significant increase in grape berry firmness between 1 and 0.5% calcium nitrate spraying compared with the control treatment.

It is worth noting that in the mechanical test of some treatments, cracking occurred due to pressure on the grape berries, which mainly occurred in the control treatment. Figure 4 shows the cracking of grape berries in the control treatment compared to the SCa treatment. In general, more cracking occurred in treatments that had low calcium concentrations, indicating the sensitivity of the fruit skin to applied pressures. Figure 5 also shows that in the control treatment (Right), a fracture state was observed almost in the middle of the curve, but in the SCa treatment (Left), no signs of fracture were seen in the curve. Cracking due to pressure is related to the sensitivity of the grape berry to applied pressure, so that after enduring pressure, the fruit skin suddenly cracked. Research has shown that potassium mainly accumulates in the skin tissues of grape berries, and during the ripening process of the berries, potassium moves from mature leaves to the fruit (Ramos and Romero, 2017). Sufficient potassium causes color in the fruit and also increases the production of polyphenols in the fruit. In general, this element plays a fundamental role in the quality of the fruit and its marketability (Griesser et al., 2017). Calcium is considered an essential element for plants that plays a fundamental role in the quality of the fruit. This element, by binding to cell wall pectin, causes better cell wall strength, thereby increasing the lifespan and shelf life of the fruit, as well as resistance to pests and diseases (Duan et al., 2022). Therefore, higher concentrations of potassium and calcium in grape berries caused better crispness and freshness, and they showed greater resistance to mechanical stress.

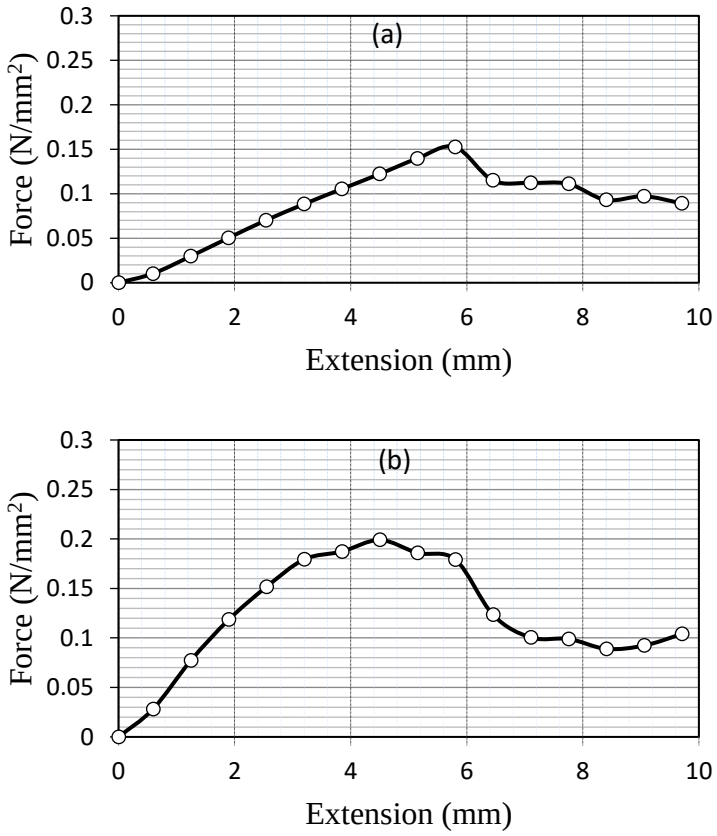


Figure 4. Mechanical strength of grape berries in the control treatment (a) and calcium sulfate spraying, SCa (b).



Figure 5. Cracking of grape berries due to mechanical pressure in the control treatment (Right) compared to the SCa treatment (Left).

4. Conclusion

The results indicated that soil application of 100 g of calcium sulfate (FCa) had a better effect on the calcium concentration of grape fruit than foliar application of 10 g of this fertilizer (SCa), although soil application of potassium (FK) and its foliar application (SK) did not have a significant difference on the potassium concentration of the fruit. It should be noted that using 10 times more fertilizer as soil application than foliar application brings much higher costs for farmers. The application of biochar increased the calcium concentration of the fruit compared to the control, although it did not have a significant effect on the potassium concentration of the fruit. By evaluating the mechanical properties of grape berries, it was found that the application of potassium increased the firmness of the grape fruit, although it reduced its flexibility. The application of calcium improved the flexibility and increased the resistance to shattering or cracking of the grape berries. It seems that increasing the concentration of both elements, calcium and potassium, in grape berries to soils increases the firmness and brittleness of the grape berries, and as a result, increases the shelf life and marketability of the grapes. However, if elemental analysis were performed on the fruit mantle and skin separately, these results would be confirmed with greater certainty. In general, the use of potassium and calcium foliar sprays is recommended due to their better absorption rate than fertilization and their lower consumption

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