



Contribution of Nano-Silica in Affecting Some of the Physico-Chemical Properties of Cultivated Soil with the Common Bean (*Phaseolus vulgaris*)

Abdullah Hassan Al-Saeedi

Department of Environmental and Natural Resources, College of Agricultural and Food Sciences, King Faisal University, P. O. Box 420, Al-Hassa 31982, Saudi Arabia
aalsaeedi@kfu.edu.sa



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ABSTRACT: Nano-silica can be used as a soil amendment to improve the physicochemical properties and crop productivity. Five rates of Nano-silica suspensions (0, 100, 200, 300, and 400 mg Si-NPs kg⁻¹ soil) were used in the current experiment to investigate the effects of Nano-silica on some chemical and physical properties added to sandy loam soil before bean plant cultivation during the 2018-2019 season. This experiment used a random complete design with three replicates. According to the findings, nano-silica rates have a substantial impact on the percentage of clay particles, cation exchange capacity (CEC), sodium adsorption rate (SAR), porosity, saturation percentage, specific surface area (SSA), total N, and Si⁴⁺. With increasing nano-silica rates salinity (EC), Ca⁺⁺, and Mg⁺⁺ decreased due to the additional uptake by plant, the bean crop yield increased with the increase of nano-silica (Si-NPs) treatments up to 200 mg.kg⁻¹ and reduced with increasing (Si-NPs) at 400 mg.kg⁻¹.

KEYWORDS: Nanosilica, CEC, pH, Bean (*Phaseolus vulgaris*), Porosity, Crop Yield, Specific Surface Area, SAR.

INTRODUCTION Silicon (Si) is the second most abundant element in the earth's crust. Although all plants contain silicon (Si) in their tissues, the concentration among plant species ranges from 0.1 to 10 % on a dry weight basis (Epstein, 2009). Silicon exists primarily in the form of mineral silicates, alumino-silicates, and silicon dioxide (SiO₂), however, most of these forms are unattainable to the plants. As the only molecular species that can cross the root plasma membrane at physiological pH, and plants can absorb silicon only in the form of mono silicic acid (H₄SiO₄), which naturally exists in the soil (Raven, 2001). However, the concentration depends on soil texture, properties, pH, organic matter, minerals present (Tubaña & Heckman, 2015), and soil moisture conditions (Ma & Takahashi, 2002; Takahashi, 1974). Many research studies have demonstrated that the positive contribution of silicon on the physical, biochemical and molecular alteration in plants alleviates plant tolerance to abiotic stress (drought, salinity, and heavy metals, et al.) and biotic stress (bacteria, fungi, viruses, insects, and herbivores) (Al-Huqail *et al.*, 2019; A. Alsaeedi *et al.*, 2017, 2018, 2019; Etesami & Jeong, 2018; Javaid *et al.*, 2019; Manivannan *et al.*, 2016; Mathur & Roy, 2020; Romero, 2011; Ullah *et al.*, 2016).

Mesoporous silica nanoparticles (Si-NPs) have fascinated researchers over the last decade due to their unique and multifaced physiochemical

properties (Jeelani *et al.*, 2020). Silica nanoparticle (Si-NPs) is non-toxic for the plant, is small in size at between 10-100 nm, has a highly specific surface area reach 350 m².g⁻¹, and has great absorption capacity by the plant cells (Asgari *et al.*, 2018; Jeelani *et al.*, 2020; Rastogi *et al.*, 2019). Rastogi *et al.* (2019) and Mathur & Roy, (2020) reviewed the benefits and the impacts of using silica nanoparticles (Si-NPs) on plant and agricultural productivity. Other studies showed a positive impact of using silica nanoparticles (Si-NPs) during the different plant growth (A. Alsaeedi *et al.*, 2017, 2018, 2019; Karunakaran *et al.*, 2013; Mathur & Roy, 2020; Rastogi *et al.*, 2019; Suriyaprabha *et al.*, 2012; Yuvakkumar *et al.*, 2011). It is known that the synthetic silica nanoparticles (Si-NPs) have the same quality and functionality as a source for the beneficial element Si similar to natural silica, but with a non-toxic effect (Asgari *et al.*, 2018; Karunakaran *et al.*, 2013; Nazaralian *et al.*, 2017; Schaller *et al.*, 2019).

As silicic acid or nanoparticles, silicon improves the nutrient availability in soil and the uptake capacity by plants. The positive correlation between phosphorus (P) availability and mobilization in soil with silicon content was demonstrated by (Neu *et al.*, 2017; Schaller *et al.*, 2019; Schaller, Frei, *et al.*, 2020). Silicon improved nutrient uptake by plants, i.e., nitrogen and phosphorus (Neu *et al.*, 2017; Seyfferth & Fendorf, 2012; Subramanian & Gopalswamy,

1991), potassium (Pati *et al.*, 2016; Singh *et al.*, 2005), iron (Mali & Aery, 2009), and macro and micronutrients as cited by (Adams *et al.*, 2020; A. Alsaedi *et al.*, 2019). Also, soil water storage capacity was significantly improved with the application of silica nanoparticles (Schaller, Cramer, *et al.*, 2020; Schaller, Frei, *et al.*, 2020). Sandy soil characterized with scanty physicochemical properties made it improper for efficient agricultural production as it resulted in low water retention and high infiltration rates, poor structural development, neglected organic matter, clay content, and easily lost nutrients via leaching (El-Saied *et al.*, 2016; Hartmann & Lesturgez, 1995).

The common bean (*Phaseolus vulgaris*) is considered the most important cultivated legume in the world. Its cultivation is of vital importance along with maize. These two food items constitute the diet of a large part of the world population, providing the largest part of the protein (Arenas-Romero *et al.*, 2013).

This work investigates the effect of applying silica nanoparticles (Si-NPs) to the plant, through the soil, on some physical and chemical properties of root zone soil.

MATERIAL AND METHODS

2.1 Greenhouse experiment:

A greenhouse experiment was carried out at the Agricultural and Veterinary Training Research Station at King Faisal University in Al-Hassa, Saudi Arabia, in 2016-2017. The soil at the experimental site was sandy (sand 99.48%, silt 0.25%, and clay 0.27%), having a pH (7.5), salinity (832 ppm), and OM (< 0.05%). Random complete design with three replicates was conducted in a greenhouse. Five treatments of synthesized hydrophilic silica nanoparticles (Si-NPs) (Aerosil 300 produced by Evonik Industries, Germany) were applied Si-NPs at rates 0, 100, 200, 300, 400 mg.kg⁻¹ to the soil before the transplanting of the common bean plant. Fertilizers (NPK) were supplied equally for all treatments according to the local program. The distance between rows was 75 cm and between two plants in the same row was 50 cm each.

2.2 Soil preparation and analysis

The soil samples were collected from the surface at a depth of 0-50 cm after harvesting. The soil was air-dried and sieved using a square hole sieve of 2 mm mesh to remove stones and other residual materials. Soil salinity, pH, cation exchange capacity (CEC), Sodium absorption rate (SAR), total nitrogen (N⁻³), Calcium (Ca⁺⁺), Magnesium (Mg⁺⁺), Sodium (Na⁺), silicon (Si⁺⁴), and saturation percentage (%) were measured according to (Frantz *et al.*, 2008; Sparks *et al.*, 2020). Soil particle analysis (clay), Specific

surface area (SSA), and porosity were quantified (Klute, 1986).

2.3 Statistical analysis

All data were analyzed statistically by the XLSTAT software package. Experiments were set up in a completely randomized design with three replicates for each treatment. When a significant difference was observed between treatments, multiple comparisons were made by Fisher's test. Significant differences were accepted at the *p* level ≤ 0.05.

3. RESULTS AND DISCUSSIONS

3.1 Physical properties

3.1.1 Clay percentage

Analysis of variance showed a significant increase in the percentage of clay among the four treatments compared to the zero Si-NPs treatment (control), as shown in Table 1 and Fig. (1). The result was highly expected due to the nanosize of the added silica. Nanoparticles, including clay and Si-NPs, increased tenfold at Si-NPs400 more than the control. Analysis of variance resulted in a highly positive significant relationship between the treatment and clay percentage *p* < 0.0001 and high correlation (R=0.98). The increase in nanomaterial in sandy soil environments adds a colloidal effect which can enhance the soil hydraulics and chemical properties (Goldberg *et al.*, 2011). As reported by Kim *et al.* (2014), nano-silica showed a highly negative zeta potential charge in the pH ranging from 3-13. Through water absorption, Si-NPs is turned into a viscous gel behaving like a clay colloid and consequently increases the bonding and connections between particles (Changizi & Haddad, 2016).

3.1.2 Porosity

High correlations were found between Si-NPs treatments and porosity (R=0.96) Figure (1B). Also, *p*=0.00013 (Table 1) indicated that the pore volume increased in the soil as we add Si-NPs. Nanoparticles accumulated in the large pores of sandy soil to create a new microporosity inside the macropores. However, that reflected positively on the overall porosity. This finding results are in agreement with the other research studies (Bayat *et al.*, 2019; Ben-Moshe *et al.*, 2013; Zhang, 2007).

3.1.3 Saturation

The saturation percentage increased by 36% from the control (Si-PNs0) to the fifth treatment (Si-NPs400). The highly significant value of *p*<0.0001 and correlation coefficient (R=0.99) (Table 1 and Fig. 1C) indicated the direct and high effect of nano-silica on the hydraulic properties of soil. This increase was due to the increase in microporosity percentages, and the increase of negative charges contributed from nano-silica particles. Many researchers similarly presented these results who reported an increase in saturation in different soil

types (Bayat *et al.*, 2019; Pérez-Hernández *et al.*, 2020; Ren & Hu, 2014; Schaller, Cramer, *et al.*, 2020).

3.1.4 Specific surface area (SSA)

Although a small quantity of Si-NPs was added to the soil, the effect was tremendously large, as shown in Figure (1D) and Table (1). The increases in SSA reached 80% (about $141 \text{ m}^2 \text{ g}^{-1}$) compared to the control with Si-NPs400. Table (1) shows a highly significant $p < 0.0001$, and the correlation coefficient (R) was equal to 0.98. SSA is the most effective property in the soil at Si-NPs treatment, leading to many Physico-chemical properties changes (Ghormade *et al.*, 2011; Pérez-Hernández *et al.*, 2020). Bayat *et al.* (2019) stated the positive effects of different nanomaterials on soil surface area using magnesium oxide MgO.

3.2 Chemical Properties

3.2.1 Salinity (EC)

Soil soluble salts depicted in Table (1) and Figure (1G) show a high negative correlation ($R = -0.99$) and a significant effect of Si-NPs treatment $p < 0.0001$, salts concentration in soil reduced as Si-NPs treatment increased. That could be due to the low level of cations and anions in the soil, as discussed later in this paper.

3.2.2 Cation exchangeable capacity (CEC)

As the value of CEC is always positively related to the specific surface area of the soil, the increase of the CEC value in this experiment was highly anticipated with the addition of nano-silica. Si-NPs400 increased the CEC up to 20% versus the control (Si-NPs=0). The analysis of the variance Table (1) showed highly significant effects from Si-NPs treatments $p < 0.0001$. Correlation, Figure (1E), is also highly significant ($R = 0.99$). Also, there is a positive high significant correlation between CEC and SSA and high correlation ($R = 0.97$) Figure (1F). The result of this paper agrees with results from other researchers who examined the effects of nanomaterials (El-Saied *et al.*, 2016; Fitriatin *et al.*, 2018; Rihayat *et al.*, 2018).

3.2.2 pH

Soil pH did not show a significant relationship with soil Si^{+4} content ($R = 0.05$) Figure (1H), although analysis of variance for Si-NPs treatments showed a slightly significant $p = 0.009$ with a correlation coefficient ($R = 0.89$) Table (1). Si-NPs200 and Si-NPs300 had the highest pH with values of 7.35 and 7.30, respectively Figure (1H). Si-NPs has a low pH ranging between 3.7-4.5. The slight increase in pH value in Si-NPs200 and Si-NPs300 could be a result of the increase in nutrient solubility in the soil such as Na^+ and decrease of some due to the excellent growth and crop yields such as Ca^{++} and K^+ content (Al-Busaidi & Cookson, 2003; Kool *et al.*, 2011).

3.2.3 Calcium and Magnesium soil content (Ca^{++} , Mg^{++})

The results shown in Table (1) demonstrated the highly significant effect of Si-NPs addition with calcium $p < 0.0001$ Figure (1A) and less significance with magnesium $p = 0.001$. Calcium content decreased in the soil as Si content increased Figure (1A). In this study, Ca^{++} and Mg^{++} content in the soil decreased as Si^{+4} content increased with negative correlation (-0.99) and (-0.95), respectively Figures (2B&D). The explanation for this could be due firstly to Si increasing the solubility and mobility of nutrients in the soil, making it readily available to plant (Aqaei *et al.*, 2020), and secondly to the improvement in the plant growth and metabolism process which maximized nutrient uptake by the root, in particular, Ca^{++} and Mg^{++} (Ditta & Arshad, 2016; Mathur & Roy, 2020).

3.2.4. Sodium (Na^+)

Data analysis of the effect of Si-NPs on the level of sodium in the soil did not show any significant difference between all treatments except Si-NPs400, which is 14% higher than others Table (1) and Figures (2E&F). It is well documented that silicon reduces the plant's sodium uptake (Ahmad *et al.*, 1992; A. H. Alsaeedi *et al.*, 2017; Yeo *et al.*, 1999). Figure (2F) shows no significant relationship between silicon content in the soil and sodium content with a poor correlation coefficient. The accumulated sodium in the soil due to root absorption selectivity under silicon treatment could be affected by the irrigation water, which leaches sodium and weakens bonds outside the root zone (Matthew & Akinyele, 2014). That could explain the nonsignificant effect of Si-NPs treatments 0-300 on sodium content in the soil.

3.2.5 Sodium Adsorption Ratio (SAR)

The high value of unutilized or excluded sodium in the soil due to the silicon's positive effect on the root absorption mechanism was reflected in SAR values (Table 1 and Fig. 2G). For this reason, Si-NPs400 recorded the highest SAR with 20% average increases compared with other treatments. Si-NPs400 showed a highly significant effect $p < 0.0001$ with all other treatments. SAR demonstrates the same behaviour as sodium in this study.

3.2.6 Nitrogen (N)

Analysis of the variance showed the highly significant effect of Si-NPs treatments on nitrogen levels in the soil $p < 0.0001$ as shown in Table (1). The relation between nitrogen and silicon content in soil showed a high correlation ($R = 0.99$) as depicted in Figures (3A&B). Si-NPs400 reported the highest value of nitrogen 0.028% with an increase of 16%, Si-NPs300 also reported a significant difference compared to zero Si-NPs with a value of 0.027%. Si-NPs200 and 100 as well showed a significant increase in nitrogen content of 0.026 and 0.025, respectively. The enhancement of nitrogen content in the soil

was referred to as the positive effect of silicon on the microorganisms in the soil, which improved the organic content in the soil (Bocharnikova & Matichenkov, 2010; Xu *et al.*, 2020) and to the positive effect of silicon in reducing the nitrogen leaching from soil (Bocharnikova & Matichenkov, 2010; Matichenkov *et al.*, 2020; Matichenkov & Bocharnikova, 2001).

3.2.7 Silicon (Si^{+4})

As expected, the value of soil silica was increased significantly as Si-NPs treatment increased with $p < 0.0001$ Table (1). Figure (3D) shows that Si-NPs400 recorded the highest silicon content, $190.74 \text{ mg kg}^{-1}$, then Si-NPs300, 200, and 100 with a value of 139.81, 95.83, and 61.11 mg kg^{-1} respectively. Many researchers report similar results for directly increasing soil content from silicon linearly with the added amount or dosage (Ma & Takahashi, 2002; Matichenkov *et al.*, 2020; Xu *et al.*, 2020).

3.3 Yield

The analysis of variance showed a significant effect of Si-NPs applications in improving the final yield of common bean (as bean) $p < 0.0001$, as indicated in Table (1). Si-NPs300 demonstrated

the maximum yield of $63.27 \text{ g plant}^{-1}$, Si-NPs 400, 200, 100, and 0 showed 59.30, 58.27, 57.26, and 55.57 respectively Figure (3E). Si-NPs400 showed a reduction of 7.2%, Si-NPs200 reduction was equal to 8.8%, Si-NPs100 also showed a reduction of 10.4%. Finally, Si-NPs0 showed a reduction in yield reached 13%. These results, supported by many references and research studies, prove silicon's positive effect in increasing the yield and physiological operation during plant life (Alsaedi *et al.*, 2017, 2019; Etesami & Jeong, 2018; Javaid *et al.*, 2019).

CONCLUSION

It can be inferred that adding nano-silica to soil increased of the clay soil content, and consequently, the saturation percentage, specific surface area (SSA), cation exchange capacity (CEC), porosity, and sodium adsorption ratio (SAR). At the Si-NPs200 rate, the improvement of these properties enhanced the total nitrogen (N) in the soil and accordingly increased the yield of the common bean. The use of nano-silica particles in soil reduced the average of salinity, soluble Ca^{2+} and Mg^{2+} .

Table 1: Mean of a square of clay, porosity, saturation, SSA, salinity (EC), pH, cation exchange capacity (CEC), soluble Ca²⁺, Mg²⁺ and Na⁺, Sodium adsorption ratio (SAR), available nitrogen (N), soluble silicon (Si⁴⁺) in the soil after pean harvesting of pean and the yield under the effect of different rates of Nano-silica amendment.

Source of variation	Degree of Freedom	Mean Squares													
		Clay (%)	Porosity (cm ³ cm ⁻³)	Saturation (g g ⁻¹)	SSA (m ² g ⁻¹)	Salinity (EC) (ppm)	CEC (cmolc kg ⁻¹)	pH	Ca ²⁺ (meq L ⁻¹)	Mg ²⁺ (meq L ⁻¹)	Na ⁺ (meq L ⁻¹)	SAR	N (%)	Si ⁴⁺ (mg kg ⁻¹)	Yield (g plant ⁻¹)
Replications	2	1.63E-06	0.000086	7.27E-06	228.54	2072.63	0.0095	0.0008	0.0005	0.0029	0.0024	0.0029	6.66E-08	99.666	1.5650
Si-NPs Treatment	4	0.00032	0.0035	0.00195	6827.47	1022792.22	0.5822	0.0129	0.1533	0.0336	0.0655	0.1704	7.56E-06	13089.95	76.4056
Error	8	4.28E-06	0.000142	2.93E-06	112.35	7689.194	0.0045	0.0018	0.0003	0.0022	0.0074	0.0053	6.66E-08	35.3692	0.3900
R (regression)		0.98	0.96	0.99	0.98	0.99	0.99	0.89	0.99	0.94	0.95	0.95	0.99	0.99	0.98
P > F		<0.0001	0.00013	<0.0001	<0.0001	<0.0001	<0.0001	0.0090	<0.0001	0.001	0.005	<0.0001	<0.0001	<0.0001	<0.0001
Significant		****	***	****	****	****	****	**	****	***	**	****	****	****	****
LSD @ 0.05		0.003	0.022	0.003	19.96	165.103	0.127	0.080	0.036	0.088	0.162	0.138	4.86E-04	11.197	1.176

LSD @ 0.05: The least significant difference at 5%

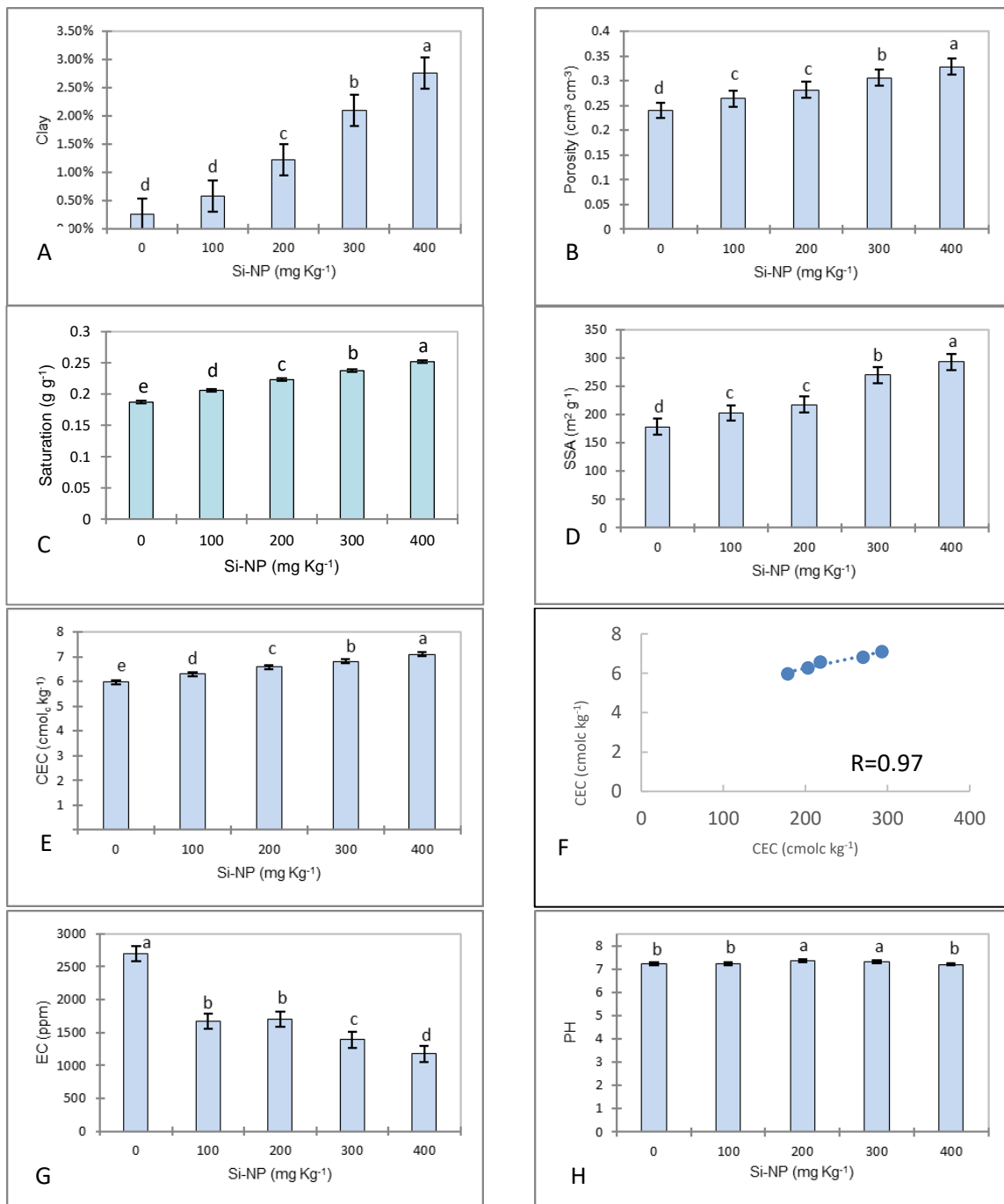


Fig. 1: The change in clay% (A), porosity cm³cm⁻³ (B), saturation cm³cm⁻³(C), specific surface area SSA m²g⁻¹(D), cation exchangeable capacity CEC (E), salinity EC ppm (G) and pH (H) under the effect of Si.NPs treatments, and correlations coefficient between CEC and specific surface area SSA (F).

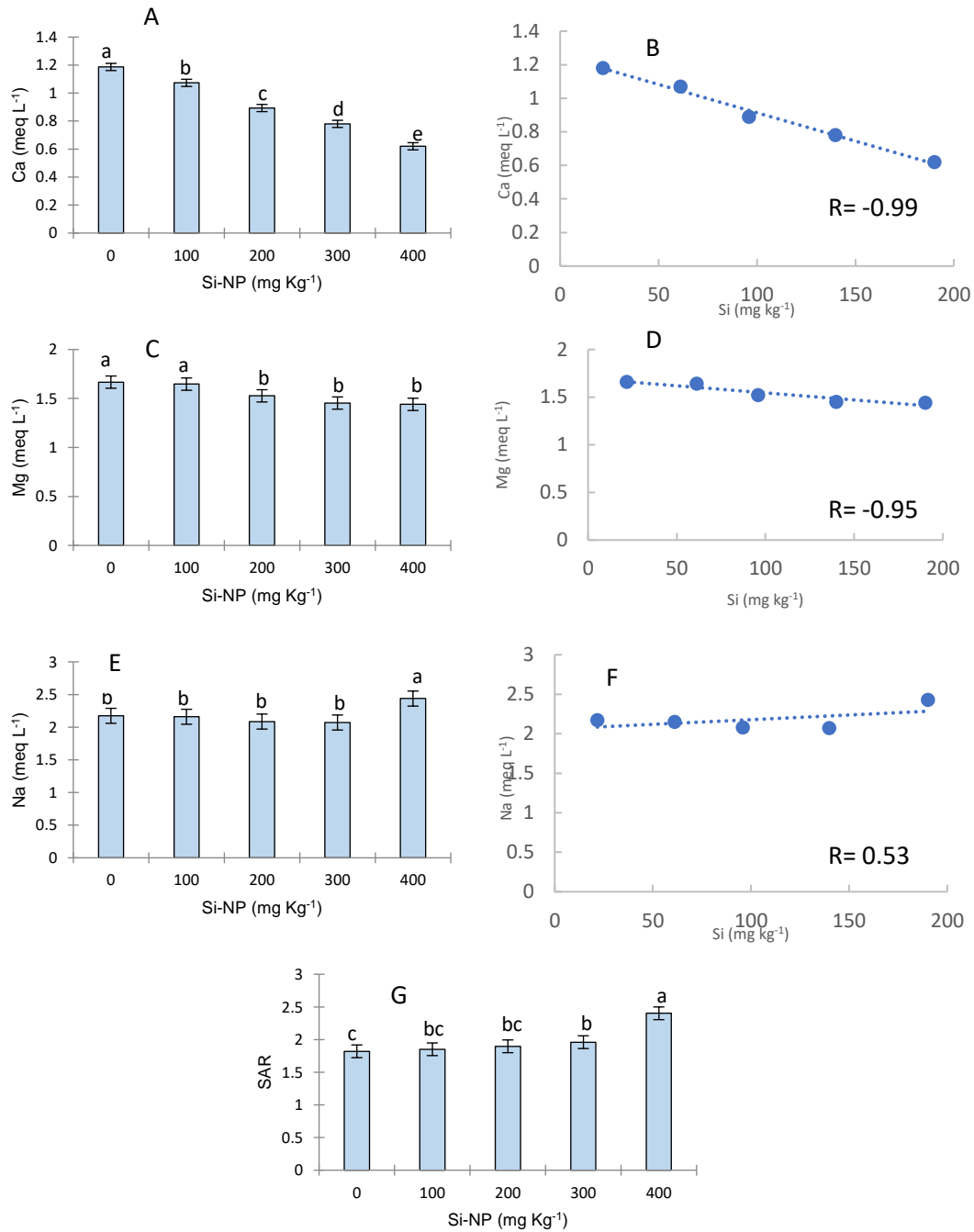
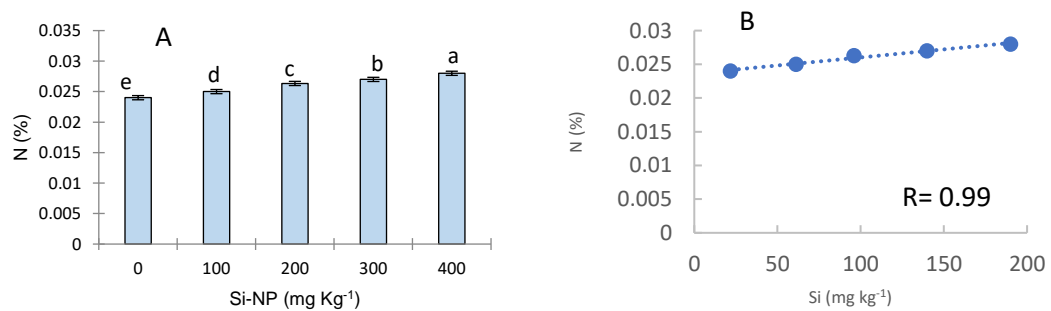


Fig. 2: The change in soluble of Ca meq L⁻¹(A) Mg meq L⁻¹ (C) Na meq L⁻¹ (E) and SAR (G) with Si-NPs treatments. While B, D, and F Figures show the correlation coefficient between Ca, Mg, and Na with valuable Si in soil, respectively meq L⁻¹ under the effects of Nano-silica application rates.



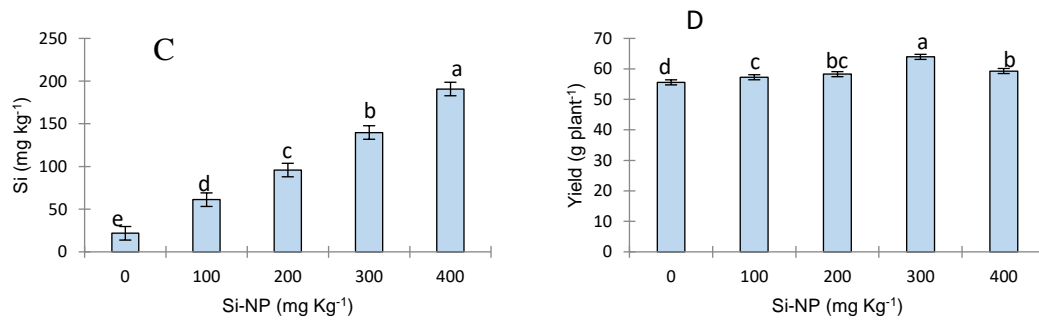


Fig. 3. The effect of Nano-silica application rates to the soil on total N% (A), soluble Si mg kg⁻¹ (C), and the yield of bean crop g plant⁻¹ (D), while the figure B indicates to the correlation coefficient between total N% and available Si mg kg⁻¹.

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المخلص العربي

مساهمة النانو سيليكيا في التأثير على بعض من الخواص الفيزيائية والكيميائية
للتربة المزروعة بالفاصوليا (Phaseolus vulgaris)

عبد الله حسن السعيدى

جامعة الملك فيصل - كلية العلوم الزراعية والاغذية - قسم البيئة ومصادر طبيعية زراعية
aalsaedi@kfu.edu.sa

في التجربة الحالية تم استخدام خمسة معدلات لمعلقات النانو سيليكيا (0 ، 100 ، 200 ، 300 ، 400 ملجم كجم⁻¹ تربة) المضافة إلى التربة الرملية قبل زراعة نبات الفاصوليا في موسم 2018-2019 لدراسة تأثير النانو سيليكيا على بعض من الخواص الكيميائية والفيزيائية. تم استخدام تصميم القطاعات الكاملة بثلاثة تكرارات في هذه التجربة. وفقاً للنتائج ، فإن معدلات النانو سيليكيا لها تأثير معنوي ايجابي على النسبة المئوية لحبيبات الطين ، والسعة التبادلية الكاتيونية (CEC) ، المسامية ،نسبة التشبع ، مساحة السطح، نسبة النتروجين الكلي، و محتوى السيليكون في التربة. كما ان المعاملات السابقة لها تأثير سلبي على درجة الملوحة، محتوى الكالسيوم و الماغنسيوم نتيجة زيادة امتصاصهما بواسطة النبات. مع زيادة معدلات النانو سيليكيا زادت جميع الخواص الفيزيائية والكيميائية قيد الدراسة. كما زاد النتروجين الكلي وإنتاجية محصول الفاصوليا مع زيادة معاملات النانو سيليكيا (Si-NP) حتى 200 جزء في المليون ثم تناقص مع زيادة Si-NP لحد 400 جزء في المليون.