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Research article

# Silicon-enhanced reduction of some heavy elements accumulation in Cowpea Plants (*Vigna unguiculata* L.)

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**Key words:** Silicon nutrition, Potassium silicate, Accumulation, Agro-mineral silicate source, Micronutrients, Heavy metals, Cowpea plants.

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**Abstract**

A field experiment was conducted using three treatments of silicon applications in order to evaluate and study the effect of foliar potassium silicate application and agro-mineral silicate (vermiculite) in soil as supplemental for Si in decreasing heavy elements accumulation in cowpea plants (shoots and roots) and their concentration in the soil. The obtained results showed that the studied treatments had a significant positive effect on Si (beneficial element) and some micronutrients (Fe, Zn and Mn). On the other hand, there was a reduction effect on some heavy elements (Cu, Ni, Pb, Cd and V) in plant and soil by using the silicate treatments as compared with control. In addition, the different silicon applications affected significantly the studied growth parameters and yield of cowpea plants.

## Introduction

In the environment, heavy elements exist in both essential and non-essential forms. At optimum level essential heavy elements such as Cu, Fe, Mn, Zn, Co, Mo, Pb, V and Ni play a beneficial role in plant growth and development. These ions readily influence role of various enzymes and proteins, arrest metabolism, and reveal phyto-toxicity [1-2]**.** Silicon has many important functions in environment, although Si is not considered as an essential plant nutrient but many plants can accumulate Si concentrations higher than essential macro nutrients [3]**.** As reported by [4], the Si content is about 200–350 g $kg^{-1}$ in clay soils and 450–480 g $kg^{-1}$ in sandy soils. Many investigations have shown that monocotyledons such as rice respond positively to an enhanced supply of Si [5]. However, beneficial effects associated with Si application have been reported also for many dicotyledons [6]. Its benefits include enhancing plant defense response against diseases, protecting plants against insect pests, increasing plant photosynthesis and growth, preventing lodging, alleviating water and mineral toxicity stresses, and improving fertilizer use efficiency [7]**.** Foliar potassium silicate is a technique in which it provides resistance to mineral stress, decreases climate stress, and improves strength and increases growth and yield [8]. Beneficial effects of silicon on uptake and in-planta mobility have been reported for both nutrient (e.g., K, Mn, Fe) and non-nutrient minerals (e.g., Na, Al, heavy metals). Further-more, Si has been reported to mitigate both nutrient deficiencies and toxicities of nutrients and non-nutrient elements [9]. Interaction between nutrients in crop plants occurs when the supply of one nutrient affects the absorption and utilization of other nutrients. Nutrient interactions can occur at the root surface or within the plant [10].

Different strategies can be taken to increase the efficient use of nutrients to maximize their benefits to the plant-soil-atmosphere system. Silicate agro-minerals amendments are defined as raw materials of mineral origin for the production of soil conditioner or fertilizer for agricultural production. These new phases are 2:1 clay minerals like vermiculite from biotite and smectite that are stable in the soil for a long-term in relation to the agronomic scales that facilitate the management of soluble cation nutrients [11].

Cowpea (*Vigna unguiculata* L. Walp.), is known as an ancient cultivar in Africa; however, it gradually started spreading via Egypt to Asia and the Mediterranean region. It is an annual herbaceous legume cultivated for its edible seeds or for fodder depending on economic or climatic constraints. Cowpea forage, both the vines and leaves, either fresh, or conserved as hay or silage, is often used for fodder [12].

The goal of this study was to evaluate the different methods of silicon applications: foliar potassium silicate and an agro-mineral silicate (vermiculite clay), and its interaction effect on some micronutrients and heavy elements on cowpea plants used for fodder to reduce the harmful effect of heavy elements in the soil and plants to introduce an eco-friendly method.

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## Material and methods

### Site and soil description

Field experiment was conducted under natural conditions in Shalaqan village, Al Qalyubia Governorate, Egypt (30°7′43″N 31°14′32″E) during the summer (May) growing season of 2017. The soil site is sandy loam classified as Typic Haplustult in the USDA system or Orthic Acrisol in the FAO system composing of 68.8 % sand, 12 % silt and 19.2 % clay with an alkaline pH of 9.45, EC of 0.24 dS $m^{-1}$and $CaCO_3$ 1.5%. Average available N, P and K from surface soil layer down to 60 cm depth at 20 cm intervals was 12, 4 and 35 mg $kg^{-1}$ soil, respectively before the initiation of the experiment.

### Soil preparation

Nursery land area was well prepared, and divided into twelve lines. Compost was added with the rate of 12 $m^3$/fed. Calcium superphosphate (15.5% $P_2O_5$) was soil incorporated during tillage operation at the rate 30 Kg $P_2O_5$/fed, potassium sulphate (48% $K_2O$) at the rate of 24 Kg $K_2O$/fed was applied immediately before first irrigation. Nitrogen in the form of ammonium sulphate (20.5% N) at rate of 60 Kg N/fed was added into two portions, half being applied before the second irrigation while the remaining portion was applied before the irrigation.

### Clay preparation

The clay mineral used in this experiment was Vermiculite. Vermiculite Sample was from El-Hafafit area in the Eastern Desert, Egypt. Its sediment was chosen from either clay sediments exploitation localities and / or from nearby radioactive mineralization occurrences. Table 1 shows some trace elements found in the vermiculite sample (analyzed in Nuclear Materials Authority Laboratories). The later shows that vermiculite has a high concentration of iron, alumina and silicon oxide reached to 2487 ppm, 15.3 % and 39.5 %, respectively.

**Table 1. Trace elements analysis of the Vermiculite sample used.**

| Element | $SiO_2$ | $Al_2O_3$ | Fe | Zn | Cu | Ni | V | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| | (%) | | (ppm) | | | | | | |
| Vermiculite | 39.5 | 15.3 | 2487 | 55 | 28 | 406 | 49 | 25 | 18 |

It was used saturated with acid and non-saturated. The saturated one was put under a small experiment to choose the best acid to be used as following: 50 grams of vermiculite finely dispersed < 2 µm was shaken for two hours at room temperature in distilled water and 0.01, 0.05, 0.1M solutions of citric and tartaric acids (These acids are representative of the various types present in humic acid and associated organic compounds in geologic and pedologic systems) then filtered, after that Si was measured in the filtered solution [13]. According to Si content (Table 2), citric acid with 0.05 M was chosen that gave $SiO_2$ (20.2 %).

**Table 2. Comparison between Si (%) by using Tartaric and Citric acid with different concentrations.**

| Concentration (M) | Available $SiO_2$ (%) | |
|---|---|---|
| | Tartaric Acid | Citric Acid |
| 0.01 | Nil | Nil |
| 0.05 | 2.57 | 20.2 |
| 0.1 | 2.53 | 18.2 |

### Experimental treatments

This experiment was complete random block design represented the treatments with three replicates for each. Each line was 120 cm long and 20 cm width. The experimental treatments were as following:

1) Control
2) Clay non-saturated
3) Clay saturated with citric acid 0.05 M
4) Foliar spray with liquid potassium silicate ($K_2SiO_3$) (10% $K_2O$, 25% $SiO_2$) was applied after the appearance of the first three leaves with the rate of 5 $cm^3$/L. Then after each week until the end of the experiment with these rates (6, 7, 8, 9, 10 $cm^3$/L), respectively.

Treatments no. 2 and 3 were applied with the rate of half Kilogram for the line of finely dispersed < 2 µm.

### Cultivation

Cowpea is a warm season crop. The time of sowing was in May. The rate is 15 to 20 kg/ha. The seed is sown by dibbling method. In layout flat bed and spacing 40 X 30 cm. planting semi-erect type with recommended spacing is 60cm × 20cm with two seeds per hill. At this spacing, up to 28 kg of seeds is required per hectare.

### Soil samples analysis

Soil samples were collected before treatments and after treatments and harvesting stage at the depth of 0–30 cm from each line. These samples were air-dried, crushed, and sieved by 2-mm sieve and preserved for analysis. Available Fe, Mn, Zn, Cu, Ni and Pb were determined according to Lindsay *et al.* [14] by shaking 20 g of soil with 40 ml of DTPA solution (pH 7.3) for 2h, filtering, and then analyzing the filtrate by atomic absorption spectroscopy. Total soluble Silicon content was determined by spectrophotometer according to Snyder [15].

### Plant Samples analysis

At harvesting stage, a random sample of three plants were chosen from each plot and prepared for chemical analysis.

These plant samples were dried at 70°C; ground using stainless steel equipment's to analyze Fe, Zn, Mn, Cu, Ni and Pb content of shoot and root. From each sample 0.5 g was digested by the mixture of sulfuric ($H_2SO_4$) and perchloric ($HClO_4$) acids (1:1) and was determined by atomic absorption spectroscopy as described by Cottenie *et al.* [16]. While, Si content was analysis by using spectrophotometer according to Snyder [15], Cottenie *et al.* [16] and Shapiro *et al.* [17].

### Parameter measured

The following plant growth parameters were measured: plant height (cm); root length (cm); fresh and dry weight of plant shoot and root (g plant$^{-1}$) and leaf area (m$^2$).

### Yield measurement

Forage yield of Cowpea plant was taken from each line from the treatment to be weighted and then represented in ton/fed.

### Infrared analysis

The samples were prepared as pellets using KBr binding material and subjected to a bruker vector spectrophotometer model FT-IR-22 Germany, in region of 4000-250 cm$^{-1}$ was used according to Russell *et al.* [18]. The IR analysis was conducted in Micro Analytical Center, Cairo University.

### Scan analysis

Most analysis was performed using low vacuum with magnification ranges from 100x to 1000x in the ESEM mode. The operating conditions were follow resolution equal to 3.5 nm at 30 KV, 25 nm at 1 KV BSE equal 10.0. This analysis was under taken in the Nuclear Materials Authority Laboratories.

### Statistical analysis

Least-significant-differences test (LSD) at $P \leq 0.05$ conducted on means of treatments to measure the considered significantly different using SAS Program (SAS 7.1, 2014) to analyze the data and separate the means.

## Results and discussion

### Characterization of soil before and after cultivation

Soil samples were characterized before and after cultivation by using scan electron microscope and IR spectroscopy. The purpose was to determine the distribution of Si before and after cultivation.

### Distribution of Si in soil sample (before and after cultivation)

Results in figure 1 of soil samples before cultivation showed the distribution of Si in soil. The ratio of Si in control was similar to that in the foliar spray of $K_2SiO_3$ sample which represented in the same EDX in Figure 1 (1 and 4), clay saturated with citric acid 0.05M and clay un-saturated were (65.2, 59.7 and 58.5)%, respectively as compared with the results obtained for soil samples after cultivation. This may be due to the absorption of Si by cowpea plants.

### Infrared (IR) spectroscopy analysis of soil samples

In the soil samples, there was no significant difference between before and after cultivation in all treatments. But, the band of soil with vermiculite saturated with citric acid 0.05M appeared at 674.96 cm$^{-1}$ (after cultivation) and 685.57 (before cultivation) cm$^{-1}$as matching with the international vermiculite that its band was at 675 cm$^{-1}$.

From figure 2 and table 3, in control sample, show that bands at 3441.35 and 3440 before and after cultivation respectively may be interoperated as- $COCH_3$ groups or may be un-bonded water molecules within the channels [19]. Also the band at 2365, 2364 may be Nitrite Oxides (N-O, N-NO) this due to the usage of nitrogen fertilizers. Bands 1633 before cultivation and 1633 after cultivation are P-O may be attributed to the usage of phosphorus fertilizers. The vibration frequencies at 786.8, 781.9 before and after cultivation are attribute to quartz.

The clay un-saturated and clay saturated with citric acid had the same interpretation and expected the bands at 674, 685 before and after cultivation, respectively and the bands at 457 before cultivation and 458 after cultivation may be interrelated to vermiculite minerals in clay saturated, 686 before cultivation and 461 after cultivation in clay un saturated as compared with international vermiculite [19].

**Table 3. Infrared spectra of Si in different soil samples.**

| Bands of soil before and after cultivation | Intensity % | Functional Group |
|---|---|---|
| 3434 - 3441 | 90.04 | $COCH_3$ stretching or water molecules |
| 2927 before cultivation in control & clay unsaturated | 101.64 | $CH_3$ groups |
| 2364 - 2373 | 115.68 | Nitrite oxide groups |
| 1629 - 1635 | 112.15 | P-O groups |
| 1430 – 1436 | 114.95 | $SO_4$ or $SO_2Cl$ |
| 772 - 786 | 120.70 | Quartz |
| 457 - 461 | 99 | May be Si – O or vermiculite |

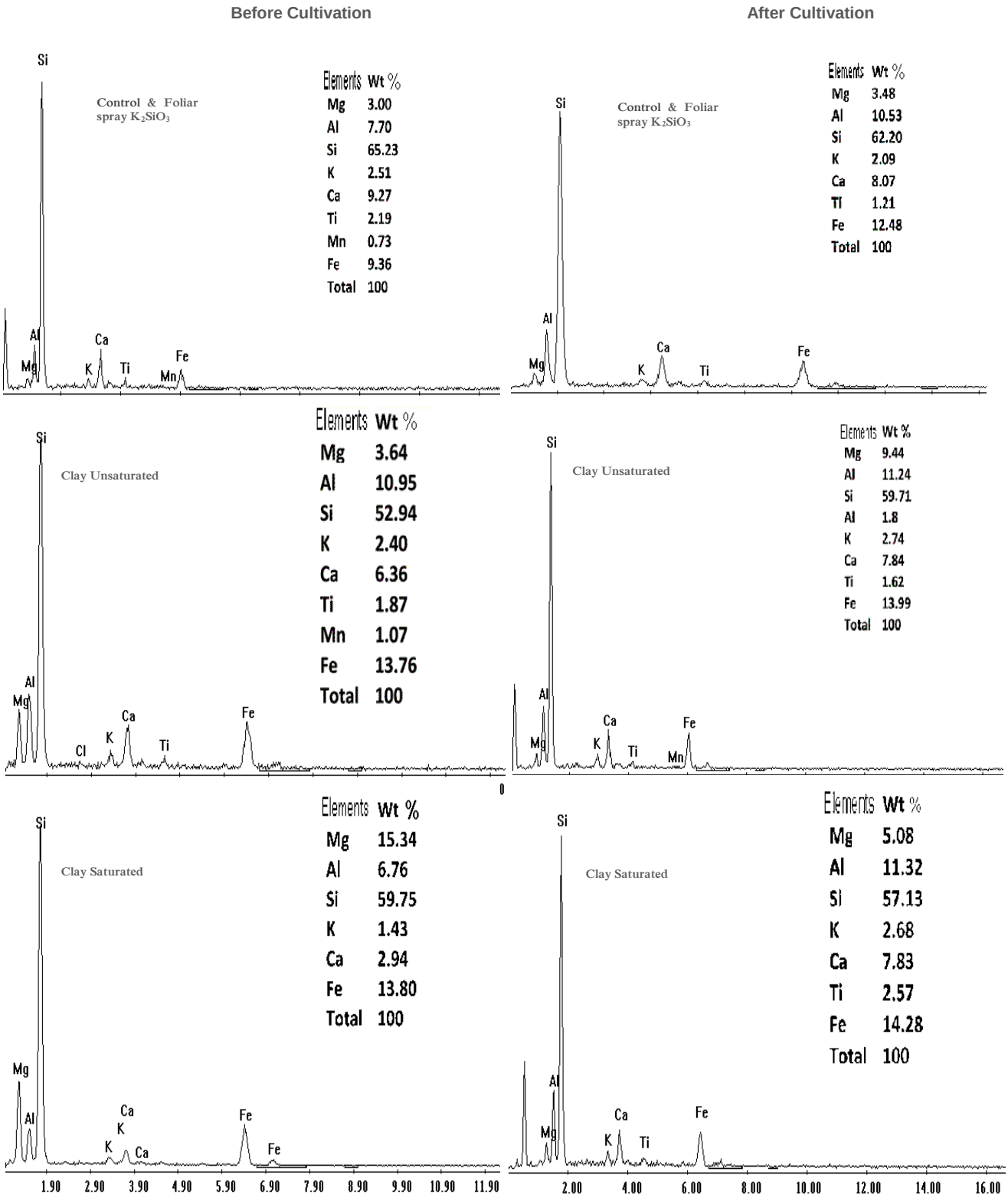



**Figure 1. Semi-quantitative ESEM analysis pattern of Si in the soil.**

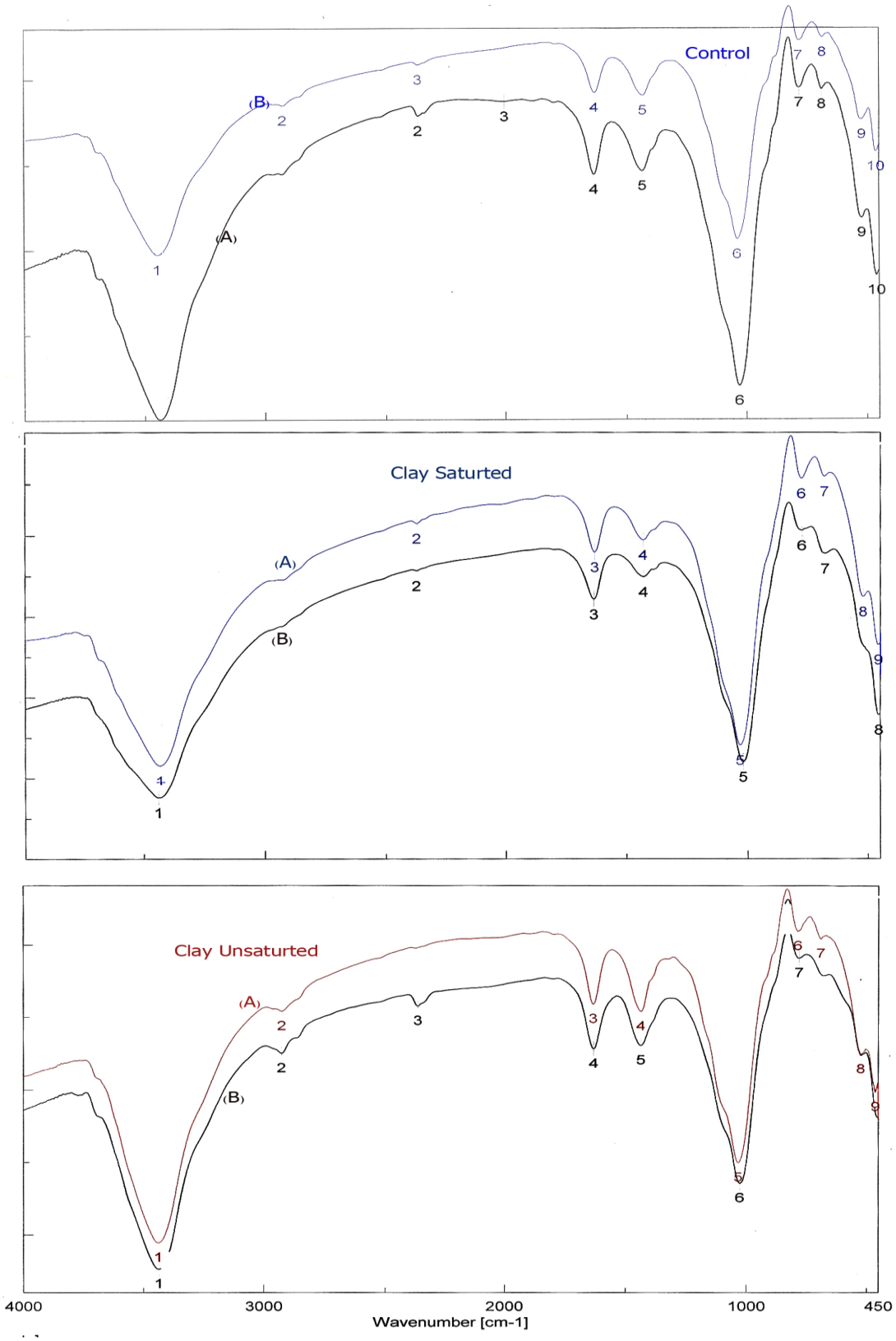



**Figure 2. Infrared spectra of soil ((A), before and (B), after cultivation), Band 7 at 674.96 (Clay saturated) (before cultivation) and Band 7 at 685.57 (Clay saturated) (after cultivation).**

## Plant characterization

### Distribution of Si in plant sample

Four represented plant samples were examined by ESEM. The EDX result in figure 3 showed a simple variation and distribution of Si and the other elements within the shoot samples of cowpea plants [20].

### Infrared (IR) spectroscopy analysis of shoot samples (Cowpea plants)

The main IR adsorption bands of the studied shoot samples represented in table 4 and figure 4.

The infrared spectrum band vibrational frequencies was present at 478.26 – 460.9 $cm^{-1}$, respectively of the two treatments (Foliar spray of $K_2SiO_3$ and clay saturated with citric acid 0.05M) as compared with the other treatments, which characteristic elemental silicon, silicon proper is represented only by the band 465 $cm^{-1}$ which overlaps with the bending band of the Si–O–Si group in $SiO_2$ as found by Zemnukhova *et al.* [21].

Also, the band of the Si–O ranged from 596.5–604.5 $cm^{-1}$ represented for all silicon treatment compared with control as found by Williams [22].

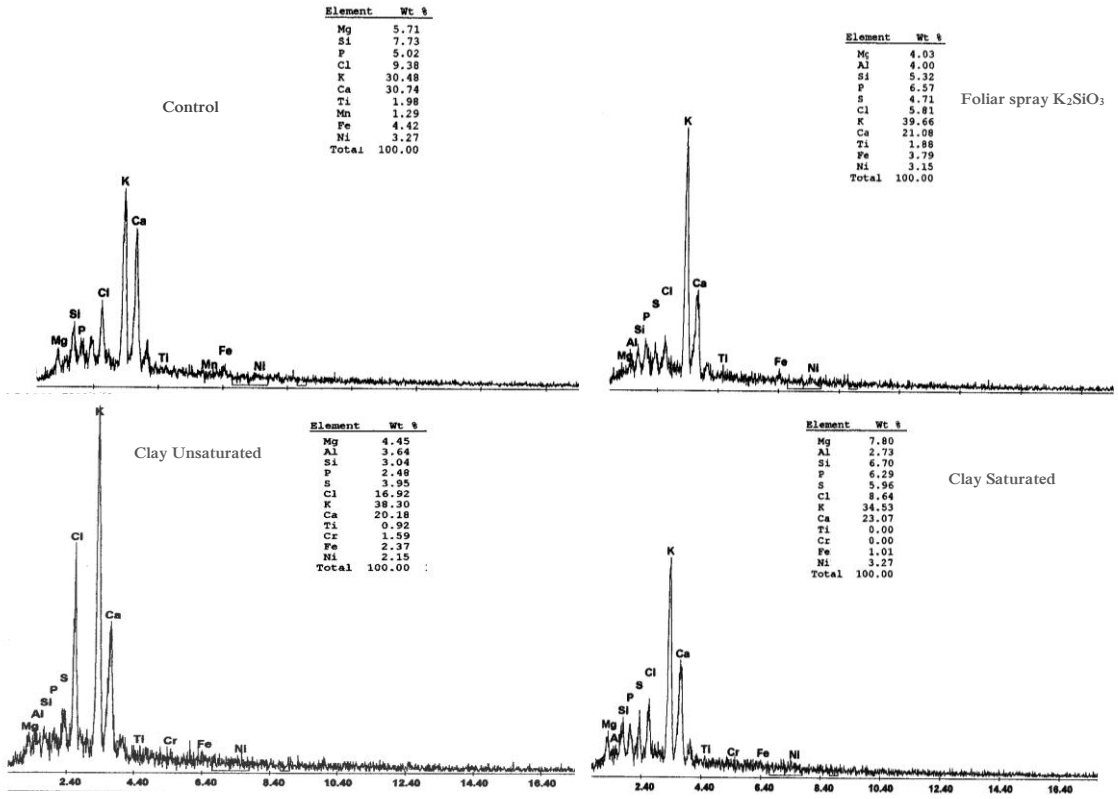



**Figure 3. Semi-quantitative ESEM analysis pattern of Si in the shoot of cowpea plants.**

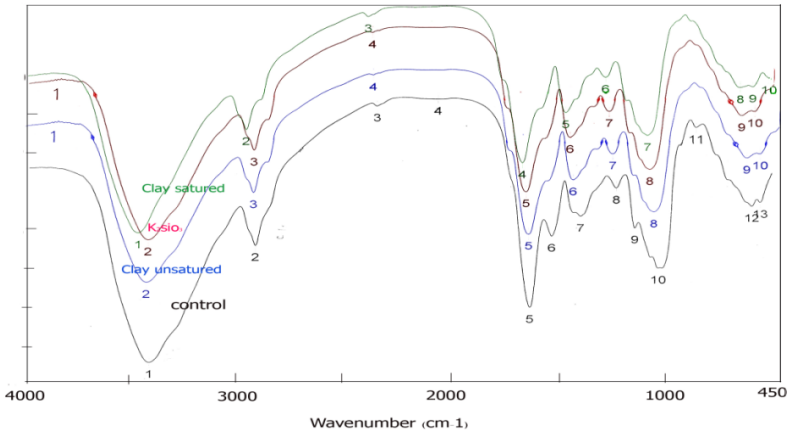



**Figure 4. Infrared spectra of Si in different shoot samples of cowpea plants. Band 8 at 603.31, 9 at 478.26 (Foliar spray), Band 8 at 596.86, 10 at 460.9 (Clay saturated), Band 9 at 604.57 (Clay unsaturated).**

**Table 4. Infrared spectra of Si in different shoot samples of cowpea plants.**

| Bands | Intensity | Functional Group |
|---|---|---|
| 3418.21-3422.06 | 78.5 | OH stretching (H- bonded). |
| 2925.48-2928.38 | 89.79 | CH stretching. |
| 2361-2370 | 105 | May be Si-H stretching or P-H stretching. |
| 1634.38– 1645.95 | 85 | May be $NH_3$ or O-$NO_2$ (Nitrate) or HOH bending. |
| 1043.3-1052.94 | 85 | Cellulose is mainly characterized. By tow strong band at 1055, 1032 $cm^{-1}$. |
| 1408.75-1435.71 | 91 | CH stretching or methyl group or $SO_2$-O. |
| 1242.9-1250.61 | 95 | C=H stretching or Nitrates O-$NO_2$. |
| 596.5-604.5 | 94 | Si-O stretching. |
| 534-537 | 92 | May be MgO or Fe. |
| 460-478 | 94 | May be Si-O-Si. |

## Growth parameters

As illustrated by table 5, foliar spray with $K_2SiO_3$ and root applied silicon (clay saturated with citric acid 0.05M) affected significantly the studied plant growth parameters as compared with control and clay non-saturated treatment. The highest mean value of plant height (184.3 cm) was observed by using the two treatments (foliar spray and clay saturated) (LSD = 5.96, $P \leq 0.05$). But the highest mean significant values of root length (22.0 cm), fresh weight of shoot (66.5 gm) and of root (2.14 gm) and dry weight of shoot (10.2 gm) and of root (0.67 gm) were obtained by using the clay saturated with citric acid treatment. On the other hand, the lowest mean significant values were observed under control.

Many reports show that silicon plays an important role in plant growth [23-24]. Also Cuong *et al.* [25] found that most of growth parameters were significantly affected by different sources of Si fertilizers. Even though from a scientific point of view, it is well established that, Si can promote plant growth and increased photosynthesis by promotion of an upright stature [26]. In general, Si is beneficial to plant increasing by increasing plant growth and biomass. This might be due to its role in increase the nutrient uptake and/or decrease in toxic metal by plants and maintenance in the structure of photosynthetic machinery [27]. Also it might be due to its responsibility to control the stomatal activity, photosynthesis and water use efficiency which ultimately results in better vegetative growth as reported by Elzbieta [28].

## Interaction effect of silicon and some essential heavy elements in cowpea plants

The content of several elements in plant (shoot and root) tissues that were significantly affected positively or negatively by Si applied treatments is reported in Table 6. Si applied treatments had a positive effect on Si, Fe, Zn and Mn in the shoot and root of cowpea plants. The highest significant mean value of Si (0.96%) in shoot was obtained by the foliar application while in root (0.31%) by using clay saturated treatment. Similar results were suggesting that the Si plant content increased by foliar application of Si [29].

In case of Fe, Zn and Mn, soil applied silicon with clay saturated gives the highest mean value in the shoot and root of cowpea plant (3660, 236, 554 ppm and 3080, 158, 668 ppm), respectively. These results were in agreements with Agostinho *et al.* [7] they reported that Si in soil has synergistic effect. On the other hand, using silicon applied treatment of clay non-saturated had a reduction effect on Cu, Ni, Pb, Cd and V in the shoot by (26.1, 54.1, 14.3, 28.3 and 62.1) %, respectively and in the roots of cowpea plants by (70, 74.2, 63.4, 13.3 and 52.8) %, respectively as compared with the control. While using silicon applied treatment of clay saturated with 0.05 M citric acid had a reduction effect on Cu, Ni, Pb, Cd and V in the shoot by (66.5, 86.6, 23.5, 28.7 and 66.3) %, respectively and in the roots of cowpea plants by (81.5, 89.6, 66.7, 18.9 and 65.9) %, respectively as compared with the control. But when using silicon applied treatment of potassium silicate foliar spray had a reduction effect on Cu, Ni, Pb, Cd and V in the shoot by (41.3, 91.9, 19.4, 28.9 and 54.8) %, respectively and in the roots of cowpea plants by (60, 92.1, 58.7, 3.5 and 64.8) %, respectively as compared with the control. One of the major effects of Si on the reduction of metal is reducing the metal uptake and transport in plants. It was reported by many researchers that Si application would enhance tolerance to heavy metals in many plant species by reducing the uptake and translocation of metals. Si-mediated decrease in Cu uptake and translocation was observed in wheat [30]. Decrease in metal translocation from roots to shoot and grains might be due to structural alterations in shoots and roots and/or co-precipitation and chelation of metals in plants [27]. Plants benefits more from soil rather than foliar application of silicon, this due to the supply of silicon to plant roots must be continuously present [31]. Other researcher has documented the benefits of foliar Si application only when plants under stress conditions [32].

Dicotyledonous plant species in general have fewer tendencies to accumulate silicon and some species may grow adequately with levels at about 0.1% Si in plant tissue. Cowpea is one of the species that of low silicon uptake ability (non-Si-accumulator) [24].

**Table 5. Some plant growth parameters of cowpea plants affected by foliar and root applied silicon.**

| Treatments | Plant height (cm) | Root length (cm) | Fresh weight (FW) | | Dry weight (DW) | |
|---|---|---|---|---|---|---|
| | | | Shoot (gm) | Root (gm) | Shoot (gm) | Root (gm) |
| Control | 171.8 | 13.3 | 53.5 | 1.40 | 7.45 | 0.34 |
| Clay non-saturated | 178.4 | 19.7 | 54.1 | 1.62 | 7.75 | 0.41 |
| Clay saturated with citric acid 0.05 M | 184.3 | 22.0 | 66.5 | 2.14 | 10.2 | 0.67 |
| $K_2SiO_3$ Foliar spray | 184.3 | 20.4 | 60.8 | 1.75 | 9.01 | 0.60 |
| LSD (5%) | 5.96 | 3.82 | 6.15 | 0.31 | 1.26 | 0.16 |

**Table 6. The effect of different silicon applications on some beneficial heavy elements contents in the shoot and root of cowpea plants.**

| Treatments | Shoot | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | (%) | (ppm) | | | | | | | |
| | Si | Fe | Zn | Mn | Cu | Ni | Pb | Cd | V |
| Control | 0.25 | 1600 | 194 | 118 | 46 | 344 | 196 | 43.2 | 548 |
| Clay non-saturated | 0.52 | 1820 | 184 | 100 | 34 | 158 | 168 | 31.0 | 208 |
| Clay saturated with citric acid 0.05 M | 0.83 | 3660 | 236 | 554 | 15.4 | 46 | 150 | 30.8 | 185 |
| $K_2SiO_3$ Foliar spray | 0.96 | 2100 | 132 | 462 | 27 | 28 | 158 | 30.7 | 248 |
| LSD (5%) | 0.319 | 132.7 | 42.7 | 33.5 | 12.82 | 86.2 | 20.1 | 6.18 | 169.18 |
| Treatments | Root | | | | | | | | |
| | (%) | (ppm) | | | | | | | |
| | Si | Fe | Zn | Mn | Cu | Ni | Pb | Cd | V |
| Control | 0.11 | 2960 | 152 | 708 | 28 | 480 | 300 | 73.8 | 452 |
| Clay non-saturated | 0.17 | 2640 | 112 | 570 | 8.4 | 124 | 110 | 64.0 | 213 |
| Clay saturated with citric acid 0.05 M | 0.31 | 3080 | 158 | 668 | 5.2 | 50 | 100 | 59.9 | 154 |
| $K_2SiO_3$ Foliar spray | 0.09 | 2100 | 90 | 156 | 11.2 | 38 | 124 | 71.4 | 159 |
| LSD (5%) | 0.099 | 187.9 | 32.5 | 53.1 | 10.17 | 80.6 | 94.8 | 7.85 | 140.89 |

**Beneficial heavy elements of Soil as affected by different silicon applications**

In the beginning of the experiment and after soil applied silicon treatments added to the soil and at harvest, soil samples had been taken and subjected to analyze the available elements that under study. From table 7, it was found that the soil applied treatments (clay saturated with citric acid 0.05M and clay un-saturated) significantly increased the amount of these elements in soil as compared with the foliar application and the control. This may be due to the initial amount of these elements in the clay (vermiculite) that used in this study. At the beginning of the experiment and at harvest, clay saturated treatment gives the highest significant mean values of Si (6.34, 4.51%) and (Fe (102, 29.8), Zn (12.3, 11.9), Mn (66.8, 13.4), Cu (1.70, 0.88), Ni (2.03, 1.50), Pb (4.40, 3.63), Cd (1.66, 1.40) and the V (199, 147) ppm, respectively. These results that obtained with clay saturated were in the same trend followed by the clay non saturated treatment as compared with the foliar spray treatment and the control. Overall the concentration of all studied elements at harvest of the experiment became less than at the beginning this due to the uptake of the cultivated cowpea plants.

Generally soils are low in available Si and would compensate from Si applications [33]. Different silicon application has a double effect on the soil – plant system as under soil treatment with bio geochemically active silicon substances optimize soil fertility through improved water, physical and chemical soil properties and maintenance of nutrients in plant available forms [34]. On the contrary side, Tubana *et al.* [31] found that Soil applied silicon sources may contain high levels of heavy elements. These applied sources will also added heavy elements to soil. The co-deposition of silica and heavy metals (e.g. Mn, Cd, Zn, Ni, Pb) in solution (in soil – root system) leads to a reduction in the concentration of free metal ions in plants. The silica-precipitated metal ions are not easily translocated, reducing their potential effect on the plant [35].

**Table 7. Effect of different silicon applications on some available beneficial heavy elements status in soil at the beginning and the end of the experiment.**

| Treatments | Before cultivation + Treatments | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | (%) | Available (ppm) | | | | | | | |
| | Si | Fe | Zn | Mn | Cu | Ni | Pb | Cd | V |
| Control | 2.53 | 18.3 | 7.95 | 12.9 | 0.75 | 0.63 | 1.18 | 1.50 | 118 |
| Clay non-saturated | 4.95 | 25.5 | 12.0 | 27.8 | 1.25 | 1.85 | 2.68 | 1.61 | 147 |
| Clay saturated with citric acid 0.05 M | 6.34 | 102 | 12.3 | 66.8 | 1.70 | 2.03 | 4.40 | 1.66 | 212 |
| $K_2SiO_3$ Foliar spray | 2.16 | 13.5 | 10.8 | 13.9 | 0.78 | 0.60 | 1.18 | 1.45 | 155 |
| LSD (5%) | 1.99 | 41.7 | 1.98 | 25.2 | 0.45 | 0.77 | 1.53 | 0.097 | 39.36 |
| Treatments | At Harvest | | | | | | | | |
| | (%) | Available (ppm) | | | | | | | |
| | Si | Fe | Zn | Mn | Cu | Ni | Pb | Cd | V |
| Control | 1.87 | 5.00 | 9.48 | 4.15 | 0.38 | Nil | 1.50 | 1.20 | 83.1 |
| Clay non-saturated | 3.70 | 11.6 | 10.1 | 7.50 | 0.65 | 0.28 | 2.70 | 1.55 | 134 |
| Clay saturated with citric acid 0.05 M | 4.51 | 29.8 | 11.9 | 13.4 | 0.88 | 1.50 | 3.63 | 1.40 | 199 |
| $K_2SiO_3$ Foliar spray | 1.28 | 5.48 | 8.03 | 2.50 | 0.23 | 0.48 | 1.55 | 1.40 | 154 |
| LSD (5%) | 1.52 | 8.61 | 1.60 | 4.81 | 0.18 | 0.65 | 1.02 | 0.144 | 48.1 |

## Forage yield of cowpea plants

After (90 days) from sowing and under different silicon application technique the fodder yield weight was taken. The highest significant mean value of fodder yield was 15.6 ton/fed (LSD = 2.059, $P \leq 0.05$) occurred with the treatment of clay saturated with citric acid treatment as shown in table 8. Meanwhile, the lowest significant mean value of fodder yield was 10.6 ton/fed occurred with the control. Whereas, it was 47.16 % increase for the clay saturated, 24.53 % increase for the foliar treatment, and 18.87 % increase for the clay unsaturated as compared with the control.

**Table 8. Means of fodder yield (ton/fed) of cowpea plant as influenced by different silicon applications.**

| Treatments | Forage Yield Weight (ton/fed) |
|---|---|
| Control | 10.6 |
| Clay non-saturated | 12.6 |
| Clay saturated with citric acid 0.05 M | 15.6 |
| $K_2SiO_3$ Foliar spray | 13.2 |
| LSD (5%) | 2.059 |

Silicon foliar application might avoid chemical or physical immobilization and function more directly, but the clay saturated has the most positive effect upon forage yield at all and preferred more than potassium silicate foliar application in economic point of view that it is a low release source of silica and the soil can be cultivated many times with the same application. Zuccarini [36] reported that silicon has a beneficial effect on growth and yield for various horticultural plant species including bean, cucumber [37], tomato [38] and Zucchini squash [39]. Silicon application may minimize problems associated with the nutrition of the plants thereby improving yield stability as found by Wu JW *et al.* [40]. Another Fabaceae plants such as cowpea used also as a vegetable for fresh production that benefits from silicon application as reported by Mali *et al.* [41]. Thus silicon fertilizers have an efficiency effect in increasing the yield of a number of crops on various soils [33].

## Conclusion

From the foregoing results, it can be concluded that: All the studied silicate applications methods had a significant positive effect on growth and yield of cowpea plants while; the agro-mineral silicate application methods using vermiculite saturated with citric acid 0.05M in soil has the best positive effect. The agro-mineral silicate application methods using vermiculite unsaturated and/or saturated with citric acid 0.05M in soil can be used to reduce the pollutant effect of some heavy elements e.g. Cu, Ni, V and Pb. Also, it can be increase some micronutrients e.g. Fe, Zn and Mn in plant and soil. The agro-mineral silicate source (vermiculite) used to improve soil characteristics and acted as a slow release for some micronutrients in the soil. So the clay minerals can remove the heavy metals from soils. Foliar of potassium silicate application achieved positive effect on growth and

yield of cowpea plants due to its function directly. It may be used in some cases to avoid chemical or physical immobilization.

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