POLYMERIZED SILICON ($SiO_2 \cdot nH_2O$) IN *EQUISETUM ARVENSE*: POTENTIAL NANOPARTICLE IN CROPS

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ABSTRACT

All technological innovation that influences research to achieve yields and counteract biotic and abiotic stress in crops should be a priority for governments and scientists around the world. Silicon nanoparticles (NpSi) in the production and protection of crops are used as a sustainable strategy. In addition to NpSi, other nanoparticles have been applicable in areas such as environmental remediation, medicine and smart sensors. There are plants that accumulate high concentrations of Si in their tissues, such as "horsetail" (*Equisetum arvense*). A recent analysis of the elemental composition of *E. arvense* in a cross section, epidermis, and total biomass indicated that the Si concentration was higher in comparison with macro and micronutrients. Elemental mapping showed that all polymerized silicon (SiO2 · nH2O) is available in the epidermis of Equisetum. Currently, our team is investigating the extraction, purification and quantification of SiNp. The lines of emerging research should be those related to the interaction of SiNp in the cell wall, concentration and intelligent application with aerial equipment in crops such as vegetables, cereals, and fruits.

Keywords: *Biotic and abiotic stress, nanoparticles, silicon, performance, epidermis.*

INTRODUCTION

The potential of nanotechnology is enormous, can greatly contribute to precision agriculture and infer in high production of crops, minimize agro-inputs, and monitoring with autonomous equipment: field diagnosis, data processing, and application intelligent in the field to correct nutrient deficiencies, pests and disease. The use of nanotechnology in agriculture is gaining importance because it contributes to develop new sustainable strategies [1]. Use of silicon (Si)-fertilizer is known as an ecologically compatible and environmentally friendly technique to stimulate plant growth, alleviate various biotic and abiotic stresses in plants, and enhance the plant resistance to multiple stresses because Si is not harmful, corrosive, and polluting to plants when presents in excess [2]. High silicon uptake, enabled by root silicon transporters, correlates with increased tolerance to many biotic and abiotic stresses [3]. The ambition of nanomaterials in agriculture is to reduce the amount of spread chemicals, minimize losses in fertilization and increased yield through pest and nutrient management [4]. This is of particular interest since beneficial effects of Si could be conferred to low accumulating plants, a strategy that could provides plants with a better resistance to biotic and abiotic stresses as a more natural approach to fend off pests and pathogens [5]. Increasing worldwide food security and challenging climatic conditions are the key components for encouraging the scientific community to focus on accelerating the growth of nanoagrotechnology [6]. In the soil solution contains silicon, mainly as silicic acid (H_4SiO_4), at 0.1-0.6 mM concentration on the order of those of postassium (K), calcium (Ca), and other major plant nutrients, and well in excess of those of phosphate (PO_4^{-3}) [7]. In general, plants with a high-silicon root or shoot Si concentration are less prone to pest attack and exhibit enhanced tolerance to abiotic stresses such as drought, low temperature, salinity and metal toxicity [8].

UPTAKE AND ACCUMULATION OF SILICON

Plant uptake silicic acid ($Si(OH)_4$) from soil solution and it is translocated to the shoots which it is deposited mainly as phytolith silica in the outer walls of epidermal leaf cells [9]. Silicon is uptake by the roots in the form of silicic acid, an uncharged monomeric molecule, when the solution pH is below 9.0 [10]. As the concentration of monosilicic acid in the cell increases, the solution becomes supersaturated, changing to form a highly polymerized gel ($SiO_2 \cdot nH_2O$) [11]. Silicon is translocated in the form of monosilicic acid through the xylem and that the concentration of monosilicic acid is high in the xylem only transiently [12]. Two different types of Si transporter (Lsi1 and Lsi2) involved in the uptake and distribution of Si have been identified[13]. Most Si is present in the soil as insoluble oxides or silicates, although soluble silicic acid occurs in the range of 0.1-0.6 mM [14]. Plants of the families Poaceae, Equisetaceae and Cyperaceae show high Si accumulation (> 4% Si), the Cucurbitales, Urticales and Commelinaceae show intermediate Si accumulation (2-4% Si), while most other species demonstrate little accumulation [15]. The Si mechanisms that underlie plants against abiotic and biotic stress are described below.

MECHANISM OF SILICON AGAINST ABIOTIC STRESS

The application of Si has been shown to alleviate negative effects of numerous abiotic stresses including salinity, heat, cold, UV-B radiation, heavy metals and mechanical stress [16]. From recent past, Si has been accepted to trigger growth-promoting effects in plants at optimal concentration and can modulate tolerance to stresses to appreciable level [17]. The Si-rich amendments rice husk and rice can be used to reduce toxicity of arsenic (As) [18]. The Si-application may increase salt tolerance in variuos important crops such as tomato, sorghum, and rice [19, 20-22]. The abiotic benefits are due to silicon´s effect on overall organ strength. Silicon is incorporated into structural components of rice cell walls were it increases cell and tissue rigidity in the plant [23]. The key mechanisms of Si-mediated alleviation of abiotic stresses in higher plants include: a) stimulation of antioxidant systems in plants, b) complexation or co-precipitation of toxic metal ions with Si, c) inmobilization of toxic metal ions in growth media, d) uptake processes, and e) compartmentalization of metal ions within plants [24]. The Si-application increase drought in rice plants through the enhancement of photochemical efficiency and adjustment of the mineral nutrient absorption [25]. The maize plants treated with Si presented not only biomass increasing but also higher metal accumulation. The deposition of silica in the endodermis and pericycle of roots seems to play an important role on the maize tolerance to Cd and Zn stress [26]. Silicon improves the water within plant tissues, which allows a higher growth rate that, in turn, contributes to salt dilution into the plant and mitigating toxic effects by salinity [27]. Silicon can alleviate freezing stress and enhance plant growth. The possible mechanisms involved may be attributed to higher antioxidant defense activity and lowe lipid peroxidation and membrane permeability, which are acquired though Si-enhanced water retention in leaf tissues [28]. Silicon not only increases tolerance to metal toxicity, but also ameliorates symptoms associated with deficiency in essential nutrients in plants, as for example K [29]. The soluble silicon in the cytosol triggers various metabolic pathways that result in the production of jasmonic acids and plant organic compounds-induced for hervivores [30]. The Si plays a pivotal role in alleviating the negative effects of alkaline stress on maize growth by impoving water status, enhancing photosynthetic pigments, accumulating osmoprotectants rather than proline, activating the antioxidant machinery, and maintainig the balance of K^+:Na^+ ratio [31]. The addition of silicon at the dose of 1.0-1.5 mM reduced some detrimental efects, of salt stress that confirms the inhibition of membrane destruction, causing a decrease in malondialdehyde (MDA) content, an increase in chlorophyll concentration and an improvement in growth parameters [32]. The suppressed concentrations of calcium (Ca) and magnesium (Mg) ions under salt stress were alleviated by the application of Si [33]. Silicon improves both quantitative and qualitative parameters in strawberries through stimulation of growth and modification of

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phenolics metabolism [34]. Silica when applied on crops in soluble form prevent oxidative stress caused due to various environmental factors which may help in better quality product and yield [35]. There is evidence that silicon nanoparticles (SiNp) were more effective that Si in reducing ion arsenate stress in maize cultivar and hybrid [36].

MECHANISM OF SILICON AGAINST BIOTIC STRESS

Interactions between Si and plant defence signal transduction pathways, specifically the key phytohormone signalling pathways, have recently been investigated [16]. Many plants armour themselves with solid hydrated amorphous silica, or opal incorporated in cell walls [37]. Structural silicon provides physical protection to plants against microbial infection and insect attack as well as redugin the quality of the tissue to the predating organisms [23]. In lettuce, tomato, and pepper plants, a beneficial effect against *Botrytis cinerea* was observed when the nutrient solution containig Si was used [38]. The physical, biochemical and molecular defense mechanisms in plants mediated by Si are the following: a) Si induces resistance against a wide range of diseases by acting as a physical barrier, which is based on pre-formed defense barriers before pathogen infection, b) Si-induced biochemical resistance during plant-pathogen interactions involves production, and regulating the complex network of signal pathways, c) Si may act at a molecular level to regulate the expression of genes involved in the defense response [39]. The enhanced diseases resistance in rice husk-treated plants appears to be positively associated with the higher accumulation of Si and Si-enhanced phenolic content and increase in enzymatic activity [40].

EXPERIMENTAL

A potential and natural source is proposed to develop Si nanoparticles from *Equisetum arvense*. The elemental composition and mapping of the silicon was performed in *Equisetum*, the sample was submerged in liquid nitrogen and processed for analysis. Using a scanning electron microscope (SEM) (Scan-ning Electron Microscope, Model 7582, England), equipped with energy-dispersive spectroscopy (EDS) (Fig. 1). The analysis of the elemental content was made directly from the epidermis of the stem (Figure 2). A third analysis was carried out to corroborate the elemental concentration of Si with respect to the other elements. The total fresh biomass was quantified (390.0 g), then it was introduced in an oven (Felissa®, model Fe-292 AD) at 60 ° C for 72 hours. The resulting dry biomass weight was (104.98 g). The dried biomass was milled in an Osterizer blender. The samples, once ground, were put into capsules for a micromolide process. The micromolino was carried out in a team (Retsch, MM400) for 9.0 minutes. To obtain a pellet of the particles of the micromolino, the sample was subjected to a hydraulic press (Retsch, PP25) at 20 tons of pressure. The resulting tablet (2 g) was placed in an aluminum mold. Relative content was determined in a scanning electron microscope (Scanning Electron Microscope, Model 7582, England) (Fig. 3).

RESULTS AND DISCUSSION

Our results demonstrate that silicon may be potentially used as a nanoparticle. In addition to *Equisetum*, there are other plant species that naturally have high concentrations of Si such as the rice plant. These nanoparticles can be used successfully of they are extracted, quantified, and applied to crops in an effective way. A challenge for agronomists, horticulturists, growers, physiologists, phytopathologists, plant breeders, biologists, microbiologists and unmanned aerial equipment for intelligent foliar application is to increase the yields of crops on the same surface. And above all that the product of economic interest is safe and of quality. The use of this silicon as a natural nanoparticle applied intelligently in crops will help reduce heat stress, cold stress, and lessen the impact of pathogens such as fungi and bacteria. The concentration of silicon deposited in *Equisetum* is high (8.67%), with respect to potassium and calcium (4.18 and 1.55%) (Fig. 1). The above was corroborated with the mapping, since it was shown that the Si is abundantly deposited in the stem surface of *Equisetum* (Fig.1a and 1b). This concentration of Si deposited on the surface of *Equisetum* can be extracted, recovered and processed for application in crops. The analysis of the elementary relative content in the different points of the Equisetum epidermis is presented in (Fig. 2). The concentration of Si in the region near the stoma was higher (13.14%) with respect to the macronutrients, this was also corroborated in the peaks of the spectra (Fig. 2a). The analysis in the region distant from the stoma showed a higher Si concentration where the values were 14.33%, higher than K 0.78%, Ca 0.14%, Mg 0.09% and S 0.06% respectively, and was also observed in the peaks of the spectra (Fig. 2b). The third analysis performed in the stoma area also showed a higher concentration of Si (15.31%) compared to the macronutrients (Fig. 2c). The foregoing demonstrates the extraction potential of this nanoparticle, and the ability of *Equisetum* to transport the Si from the root to the epidermis. The elemental analysis of the total biomass in *Equisetum* showed that the concentration of Si (6.2%) was higher than N, P, K, and Ca respectively (Fig. 3). The concentration in this third analysis differs with the concentration of the mapping and spectrum (Fig. 1 and 2), this may be due to the fact that the total biomass of *Equisetum* was considered. However, Si remains predominant in the sample.

Composition	K	Ca	Mg	S	Si
Relative content (%)	4.18	1.55	0.41	0.31	8.67

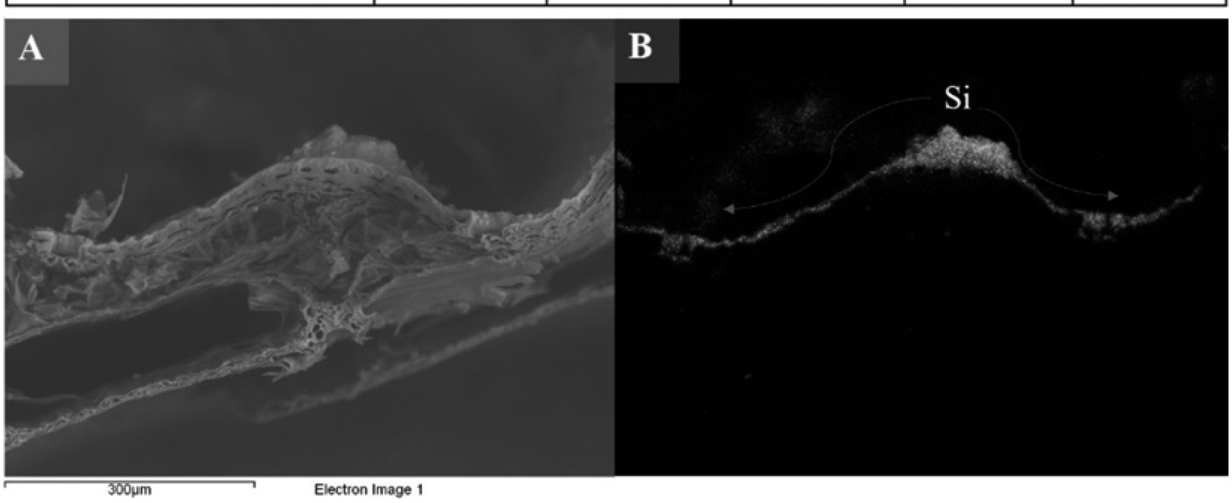
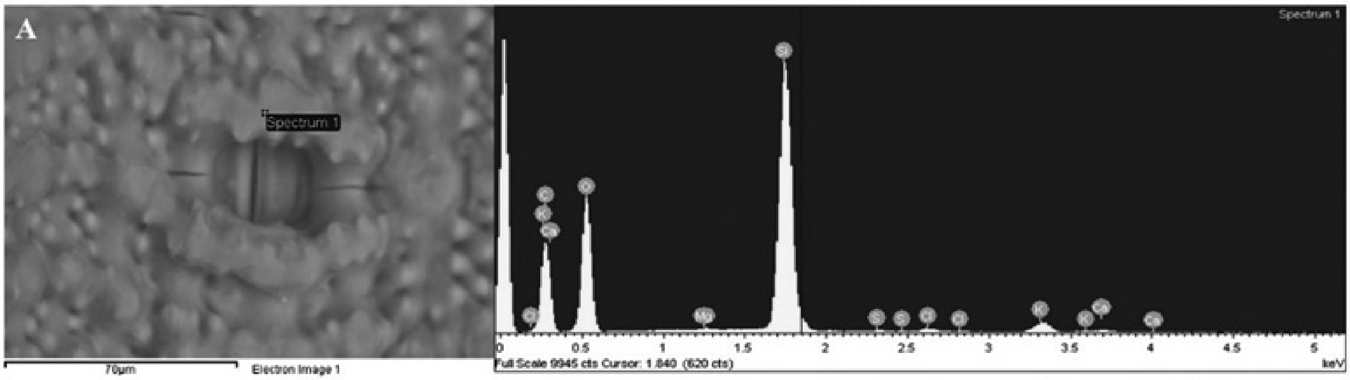
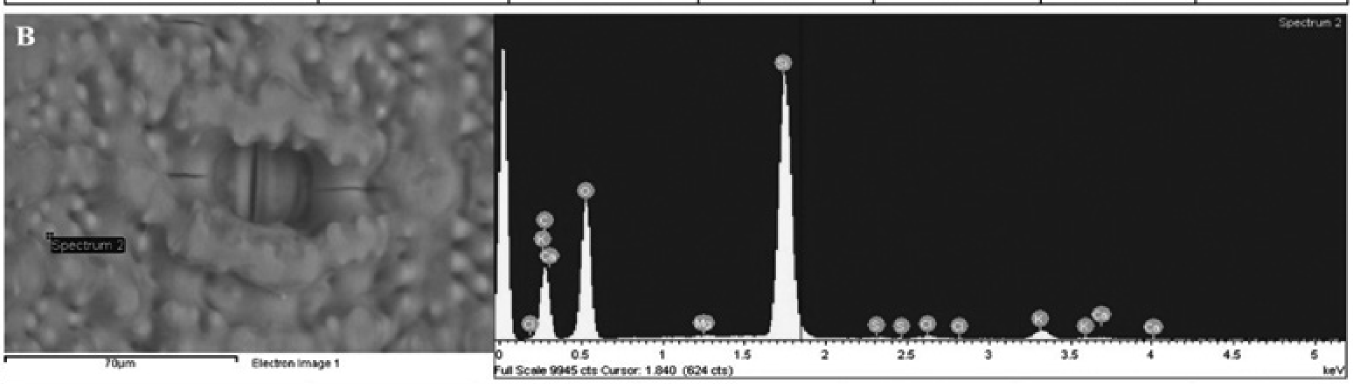


Figure 1: SEM-EDS analysis of the elemental composition, (a) cross se tion of Equisetum arvense, and (b) elemental content of silicon in the mapping.

Composition	K	Ca	Mg	S	Si	Cl
Relative content (%)	0.76	0.17	0.11	0.07	13.14	0.23



Composition	K	Ca	Mg	S	Si	Cl
Relative content (%)	0.78	0.14	0.09	0.06	14.33	0.19



Composition	K	Ca	Mg	S	Si	Cl
Relative content (%)	1.34	0.30	0.10	0.11	15.31	0.29

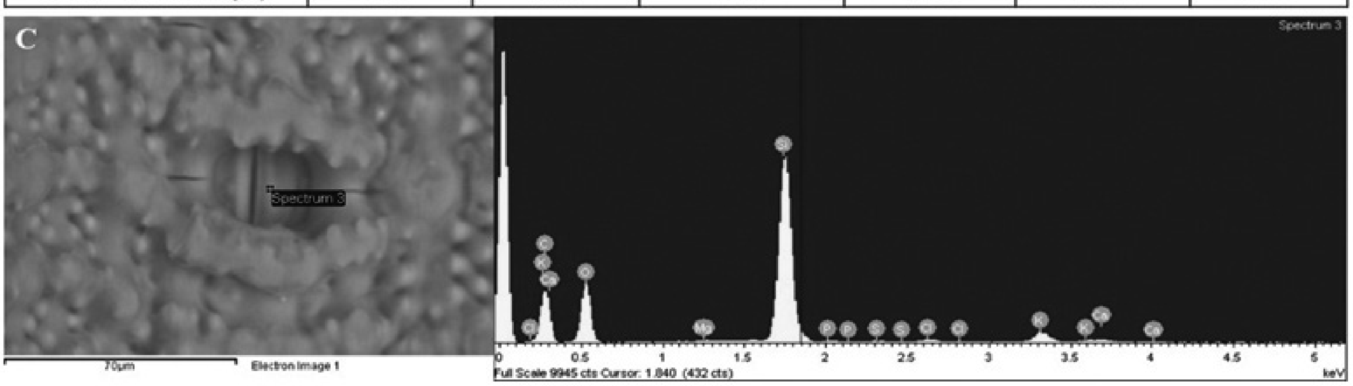


Figure 2: SEM-EDS analysis of relative content, (a) region of the stoma, (b) region of the stoma, and (c) in the stoma area.

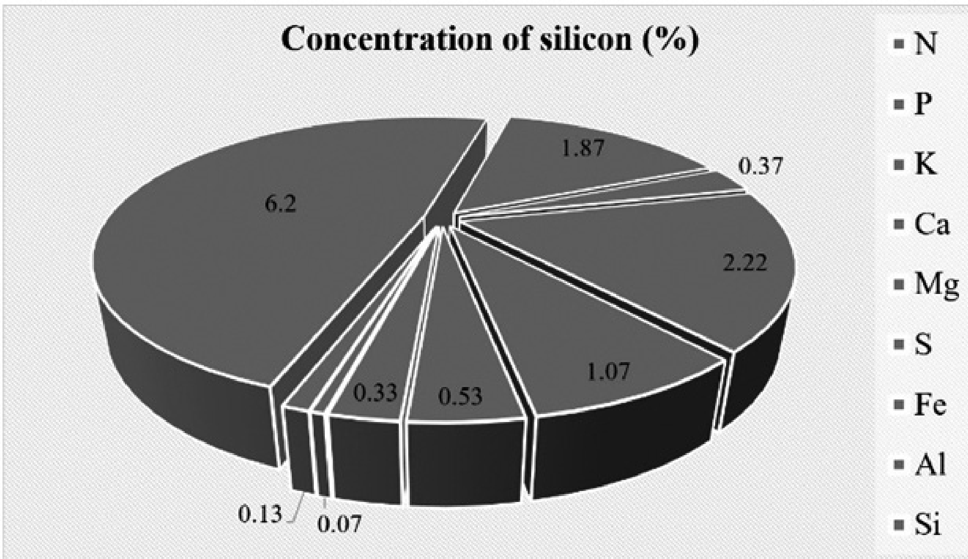


Figure 3: Concentration of silicon in the total biomass of *Equisetum arvense*.

The application of nanoscale fertilizers in found to be superior than bulk silica as soil amendment. The nanosilica at 15 kg ha^{-1} may render the optimal regime for improved growth during field application for corn [41]. For example, with 8 g L^{-1} of nanosilicon dioxide (nSiO_2: size- 12 nm) improved percent seed germination, mean germination time, seed germination index, seed vigour index, seedling fresh weight and dry weight in tomato [42]. Effect of NPs varies from plant to plant and depends on their mode of application, size, and concentrations [43]. The foliar application of nano-SiO_2 increase the production systems of crops under unfavourable environmental conditions [44]. Foliar sprays with silicates are effective as pesticides, while silicic acid sprays increase growth growth and yield and decrease biotic and abiotic stresses [45]. With the use of nanotechnology, it has been improved the quality of modern agricultural practices by them technical, safer and improved quality in agricultural products nutritious [46].

NEW CHALLENGES AND DIRECTION

Development of studies in the field of nanoparticles such as Si and its practical application must be carried out. The technological improvements that optimizing the good development and growth of crops in the face of biotic and abiotic stresses are a challenge. The population in Mexico, will require an increase in the production of food (vegetables, grains, cereals, and fruit), and that these are rich in mineral, metabolites, and antioxidants. Once the nanoparticles have been developed as nanofertilizers, they must be rigorously evaluated in the field. Knowing its kinetics and the impact it has on the physiology of crops and especially that they do not have toxic effect for final consumers. The nanotechnology based delivery of nanoparticles has given promising results for plant disease resistance, enhanced plant growth and nutrition via site specific delivery of fertilizers and other essential nutrients with the help of controlled release formulations of nanoparticles [47]. Nanotechnology has the potential to provide solutions for fundamental agricultural problems caused by conventional fertilizer management [48]. Besides, the nanotechnology offer opportunities to make food production more sustainable by providing better sensors for monitoring physical, chemical, or biological properties and processes. Technologies for controlling pathogens to increase food safety and minimize food waste [49]. The nanofertilizers such as N, P, K, Fe, Mn, Zn, Cu, Mo and carbon nanotubes show better release and targeted delivery efficiency [50]. The nano-nutrition for the provision of nano-sized nutrients for the crop production in a challenge for new research in the field [51]. Nanotechnology offers great potential to tailor fertilizer production with the desired chemical composition, improve the nutrient use efficiency that may reduce environmental impact, and boost the plant productivity [52]. It is necessary to study multiple mechanisms at physiological, biochemical, and molecular levels are involved for penetration, acquisition, and in plant transport of nanoparticles [53]. Future studies should facus on the generation of novel NPs that can either enlarge or induce pores in cell walls to facilitate the transfer of NPs across cell walls and other barriers [54].

CONCLUSIONS

Silicon polymerized as a nanoparticles in *Equisetum arvense* is a potentially usable source. The analysis of elemental content shows that Si is present in greater concentration in the epidermis. The extraction, purification and quantification of nanoparticle will be used as a nanofertilizer to soil and foliar. The need arises to open new lines of research to know the interaction of the nanomaterial with the cell, the adequate concentration, the companion ion for a greater assimilation, and the intelligent way of application in the crops, for a greater efficiency, and sustainable use.

ACKNOWLEDGEMENTS

Laboratorio de Análisis y Diagnóstico del Patrimonio – LADIPA, El Colegio de Michoacán, A.C, for the facilities provided and the analyst Esteban Sánchez-Rodríguez.

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